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PREFACE

In this volume are the papers and discussions on Iron and Steel that were presented at the Lake Superior meeting, August, 1920, the New York meetings of 1921 and 1922, and the Wilkes-Barre meeting, September, 1921; also Proceedings of the New York meeting, February, 1922.

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PROCEEDINGS

New York Meeting, 1922

THE 125th meeting of the Institute was held in New York, Feb. 20–23, 1922, inclusive, and was the most successful annual meeting of the Institute; there was a larger registration, there were more sessions of importance, and a greater number of sessions, than in any previous year. The total registration was 1331, comprising 351 New York members, 393 visiting members and 587 guests.

At the annual business meeting of the Institute, held on Tuesday, Feb. 21, with President Ludlow presiding, there was a much larger attendance than usual.

Section III of Article 6 of the Constitution was amended by changing the word "six" to the word "eight," requiring eight for a quorum of the Board of Directors necessary to transact business.

TECHNICAL SESSIONS

The technical sessions were greater in number than ever before and overflowed the ordinary space at the service of the Institute for this purpose; several sessions were held in the quarters of the other societies, which gladly donated rooms for this purpose.

The Symposium on Foreign Oil Possibilities and Details of the Oil Industry drew the largest attendance and occupied the center of interest. The oil sessions overflowed their quarters on the first day and had to be transferred to the Auditorium. Only the papers presented at the last oil session had been prepared for distribution, because the discussion at the earlier sessions, in many cases, dealt with delicate questions of international policy, and for the same reason none of these sessions was reported, as were all of the other sessions. Some of these papers were published later.

The Mining Methods Committee, engaged as it is in the collection of data from all of the big mines of the United States to answer the questions involved in the choice of mining methods with all the necessary controlling factors, had a continuous session of well-attended meetings throughout the convention.

The Institute of Metals Division, in addition to two of the largest sessions it has held since affiliating with the Institute, conducted the lecture by Prof. Wilder D. Bancroft on Colloid Chemistry and Metallurgy, which attracted a great deal of interest.

The Iron and Steel Sessions were in part devoted to memorials of the late Prof. J. W. Richards, who was for so long the very able and efficient chairman of the Iron and Steel Committee.

The Safety Sessions were joint sessions of the Mining Section of the National Safety Council and the Industrial Relations Committee of the Institute, and another notable joint session was a meeting of the Mining and Metallurgical Society of America with the Institute, at which papers and discussions on Waste in the Mining Industry were presented. These constituted the feature of the March, 1922, number of MINING AND METALLURGY.

Another innovation at this meeting was a Local Section Convention, at which the chairmen and secretaries of the various local sections, or in their absence their representatives, gathered to discuss local section problems as related to the Institute and its problems as related to the local sections. The new president of the Institute, Col. Arthur S. Dwight, presided. This convention proved to be such an interesting feature that the one session provided for its initial meeting was entirely inadequate, and it is hoped and expected that this will become a permanent feature of the Institute meetings. Technical sessions were as follows:

Symposium on Foreign Oil Possibilities and Details of the Oil Industry

Chairman, Ralph Arnold

TUESDAY MORNING, FEB. 21

Introductory Remarks. Ralph Arnold.
Addresses on: Oil Reserves of United States. David White.
Canada. Ralph Arnold and Walter A. English.
Mexico. V. R. Garfias.
West Indies, except Trinidad. A. H. Redfield.
Central America. A. H. Redfield.
Colombia. Chester W. Washburne and K. D. White.
Venezuela, the Guianas, and Trinidad. Ralph Arnold, B. Bryan, and G. A. Macready.

TUESDAY AFTERNOON

Addresses on: Oil Reserves of Peru and Ecuador. V. F. Marsters.
Bolivia.* C. W. Washburne.
Argentine and Chile.* E. W. Shaw.
Brazil. J. C. Branner.
Japan. J. Morgan Clements.
China and Siberia. Eliot Blackwelder.
Philippines. W. E. Pratt.
Galicia.* R. N. Ferguson.
Europe, Africa, Asia, Australia, New Zealand, and East Indies.* A. Beeby Thompson and Robert Anderson.

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* Not printed by the Institute.

WEDNESDAY MORNING, FEB. 22

Addresses on: Suggestions for Stabilizing the Oil Industry.* Henry L. Doherty.
Oil Laws of Latin-American Countries. Edward Schuster and Frank Feuille.
What the State Department Can do to Aid in Foreign Oil Development. Lester H. Woolsey.

WEDNESDAY AFTERNOON

Future Demands on Oil Industry of United States. By J. E. Pogue.
Time to Pay out as a Basis for Valuation of Oil Properties. By W. Irwin Moyer.
Production Problems of Grass Creek Oil Fields. By E. L. Estabrook.
Possible Origin of Oil. By Colin C. Rae.
Subsurface Conditions on Portion of Arches Fork Anticline. By K. Cottingham.

Mining Sessions

MONDAY AFTERNOON, FEB. 20

Chairman, B. B. Gottsberger

Sampling and Estimating Ore Deposits. Introductory Remarks by B. B. Gottsberger.
Diamond-drill Sampling Methods. By R. D. Longyear.
Sampling and Estimating Disseminated Copper Deposits. By I. B. Joralemon.
Sampling and Estimating Iron-ore Deposits:
Lake Superior Iron District.* By J. F. Wolff, E. L. Derby, and W. A. Cole.
Gogebic Range.* By J. F. Wolff.
Menominee Range.* By J. F. Wolff.
Marquette Range.* By R. W. Bowers.
Sampling and Estimating Zinc and Lead Orebodies of Mississippi Valley. By W. F. Boericke.
Organization of Mine Sampling at Anaconda. By W. B. Daly and F. A. Linforth.

TUESDAY MORNING, FEB. 21

Chairman, William Kelly

Storage-battery Locomotive as Applied to Mine Haulage. By Charles E. Stuart.
Electric Haulage Systems in Butte Mines. By C. D. Woodward.
Handling Ore in Mines of Butte District. By H. R. Tunnell.
Power Distributing System for Deep Metal Mines. By C. D. Woodward.
Effect of Rate of Production on Profits. By W. O. Hotchkiss.

TUESDAY AFTERNOON

Chairman, E. E. Hunner

Introductory Remarks on Work of Mining Methods Committee.* By John E. Hodge.
Mining Engineers.* By Arthur Thacher.
Recovery of Tonnages and Values under Various Mining Methods.* By Henry Krumb.
Nomenclature of Mining Methods.* By F. W. Sperr.

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*Not printed by the Institute.

General Outlines for Obtaining Data.* By E. E. Hunner.
Discussion by Messrs. Charlton, Gillies, Hotchkiss, Jackson, Kelly, Kemp, Linton, Raymond, Sebenius, Stoek, Westervelt, Yeatman.
Spies Open-stope System of Mining. By S. R. Elliott.
Stope Cost Records and Mine Contracts of Anaconda Copper Mining Co. By C. I. Berrien.
Steam-shovel Operations at Bisbee, Ariz. By H. M. Ziesemer and George Mieyr.
Mining Methods at the Ashio Copper Mine. By M. Otagawa.

WEDNESDAY MORNING, FEB. 22

Chairman, Howard N. Eavenson

Systems of Mining in Pocahontas Coal Field, and Recoveries from Them. By T. H. Clagett.
Discussion by Messrs. Gay, Haas, Peltier, Ramsay, Cox, and Newbaker.
Can Anthracite Mines be Operated Profitably on More than One Shift? By D. C. Ashmead.
Some Considerations Affecting the Extraction of Bituminous Coal in American Mines. By H. H. Stoek.
Mine Timber Preservation.* By R. R. Horner and G. M. Hunt.
Underground Fire Prevention by the Anaconda Copper Mining Co. By E. M. Norris.
Mine Fires and Hydraulic Filling. By H. J. Rahilly.

Safety Sessions

Wire Ropes and Hoisting †

MONDAY AFTERNOON, FEB. 20

Joint Chairmen, B. F. Tillson and H. F. Lunt

Safety Practice for Hoisting Ropes. By R. M. Raymond.
Use of Wire Rope in Mining Operations. By J. F. Howe.
Wire Rope and Safety in Hoisting at Butte Mines. By W. N. Tanner and F. C. Jaccard.
Safety Devices for Mine Shafts. By Rudolf Kudlich.

Ventilation

TUESDAY MORNING, FEB. 21

Joint Chairmen, B. F. Tillson and H. F. Lunt

Efficient Ventilation of Metal Mines. By D. Harrington.
Ventilation of Butte Mines of Anaconda Copper Mining Co. By A. S. Richardson.
Coal-mine Ventilation. By J. J. Walsh.

General

WEDNESDAY AFTERNOON

Joint Chairmen, B. F. Tillson and H. F. Lunt

Bureau of Safety of Anaconda Copper Mining Co. By C. W. Goodale and J. L. Boardman.
Electric Signal Installation in Butte Mines. By C. D. Woodward.
An Inventory of Results of Accident Prevention in Utah. By C. A. Allen.

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* Not printed by the Institute.

† Joint Session of Mining Section of National Safety Council and Industrial Relations Committee of the Institute.

Industrial Relations Session

TUESDAY AFTERNOON, FEB. 21

Chairman, Robert Linton

Reports of Sub-Committees on:

Americanization.	Housing and Recreation.
Cripples in Industry.	Mental Factors in Industry.
Education.	Prevention of Illness.
Employment.	Safety.

Preservation of Natural Scenery and Attractiveness of Mining Camps. By George F. Kunz.

Non-metallic Session

WEDNESDAY MORNING, FEB. 22

Chairman, H. Ries

Non-metallic Mineral Filler Industry. By W. M. Weigel.
Undesirable Diversity in Non-metallic Mineral Products. By Oliver Bowles.
Potash Reserves in West Texas. By David White.

Institute of Metals Division

MONDAY AFTERNOON, FEB. 20

Chairman, W. H. Bassett

Results Achieved by Corrosion Committee of British Institute of Metals.* By E. E. Thum.
Experiments with Sherardizing. By Leon McCulloch.
Spectrum Analysis in an Industrial Laboratory. By Wm. H. Bassett and C. H. Davis.
Arsenical Bearing Metals. By Harold J. Roast and C. F. Pascoe.

TUESDAY AFTERNOON, FEB. 21

Chairman, W. H. Bassett

Business Session of the Division.
Slip Interference Theory of Hardening of Metals.* By Zay Jeffries and R. S. Archer.
Crystal Structure of Solid Solution. By Edgar C. Bain.
Thermal Expansion of Copper and Some of its Important Alloys (Bureau of Standards).* By P. Hidnert.
Thermal Expansion of Nickel, Monel Metal, Stellite, Stainless Steel and Aluminum (Bureau of Standards).* By P. Hidnert and W. Souder.
Studies on the Constitution of Binary Zinc-base Alloys. By Willis McG. Peirce.

Iron and Steel Sessions

WEDNESDAY MORNING, FEB. 22

Chairman, Bradley Stoughton

This session was in memory of Prof. J. W. Richards.

Application in Rolling of Effects of Carbon, Phosphorus and Manganese on Mechanical Properties of Steel. By W. R. Webster.

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*Not printed by the Institute.

Acid Open-hearth Process for Manufacture of Gun Steels and Fine Steels. By W. P. Barba and Henry M. Howe.

Effect of Sulfur and Oxides in Ordnance Steels. By W. J. Priestley.

Electrolytic Deposition of Iron for Building up Worn or Undersized Parts. By D. R. Kellogg.

WEDNESDAY AFTERNOON

Chairman, C. P. Perin

Effect of Time in Reheating Quenched Medium-carbon Steel Below the Critical Range. By C. R. Hayward, D. M. MacNeil, and R. L. Presbrey.

Effect of Quality of Steel on Case-carburizing Results. By H. W. McQuaid and E. W. Ehn.

Malleableizing of White Cast Iron. By Arthur Phillips and E. S. Davenport.

Joint Meeting with Mining and Metallurgical Society

WEDNESDAY AFTERNOON, FEB. 22

Chairman, Allen H. Rogers, President, M. & M. S. A.

Waste Involved in Preliminary Investigation of Mineral Deposits. By H. Foster Bain.

Factors in Management of Mining Properties Which Lead to Loss and Waste. By Pope Yeatman.

The Elimination of Waste and the Improvement of Efficiency. What are the Economic Fundamentals? By W. R. Ingalls.

Waste in Coal-mining Industry. By Edwin Ludlow.

The Engineer's Relation to Elimination of Waste in Mining. By J. Parke Channing.

Local Section Convention

WEDNESDAY AFTERNOON, FEB. 22

Chairman, Arthur S. Dwight

Informal Discussion of Matters of Interest to the Sections, and Address by L. W. Wallace on the Federated American Engineering Societies.

THE SMOKER

The annual smoker was held on the fifth floor, Monday night, which was well filled. A wireless telephone furnished musical numbers from a broad-casting station west of the Hudson River. These numbers were interspersed with fake wireless messages, which were telephoned from an outside room, perpetrating various jokes on Institute members and the more or less hectic happenings of the past year, particularly with reference to publication.

The Entertainment Committee offered a prize for the best limericks, and many of these, which were projected on the screen, elicited much laughter and applause.

THE BANQUET AND OTHER SOCIAL EVENTS

On Tuesday evening, the large room on the fifth floor was filled with

members and guests to see two moving pictures, entitled "Mexico and Its Oil" and "Through India with the Duke of Connaught, including a visit to the Tata Iron and Steel Works."

On Wednesday evening the Institute's annual banquet and ball were held in the grand ballroom of the Pennsylvania Hotel; 645 covers were laid, making it within seven of the largest banquet the Institute has held at its annual meeting. George Otis Smith, of the U. S. Geological Survey, was toastmaster and the only two speakers were the retiring and newly elected presidents, Edwin Ludlow and Col. Arthur S. Dwight.

Senator William A. Clark again generously opened his art galleries to the members and guests of the Institute. More than 500 tickets were issued at the Registration Desk. As usual, a delightful tea at Senator Clark's home followed the inspection of his art collection.

The Womans' Auxiliary had a longer and more attractive, and probably more strenuous, program than usual.

The fourth day of the convention was devoted to excursions to various industrial plants in New Jersey. A special train from Jersey City took the oil group to the Bayway plant of the Standard Oil Co. (N. J.); the steel group to the plant of the Crucible Steel Co. of America, Harrison, N. J., and the copper group to the Chrome plant of the U. S. Metals Refining Co. About two hours was allowed for seeing these plants. The special train collected the different groups and took them to Perth Amboy, N. J., where they were entertained at luncheon by the Industrial Association of that city.

The gymnasium at the Y. M. C. A. had been converted into a large dining room, seating 400 people, and a delicious luncheon was served by ladies of Perth Amboy.

In the afternoon, many of the ladies were entertained at the Raritan Yacht Club, and a few accompanied the members and men guests on visits to the copper-fabricating plant of the Standard Underground Cable Co.; the copper-refining plant of the Raritan Copper Works, where oil is largely used as fuel; the roofing plant of the Barber Asphalt Paving Co. at Maurer, N. J., or the refractory plant of Henry Maurer & Son.

The groups reassembled on the special train, and reached New York at 6 p. m.

PAPERS

Chemical Equilibrium between Iron, Carbon, and Oxygen

By A. Matsubara,* *Rigakushi*, Kioto, Japan

(New York Meeting, February, 1921)

The problem of the equilibrium between iron, carbon, and oxygen was first carefully investigated by E. Baur and A. Glaessner,[1] who determined the equilibrium conditions of the two reactions

$$Fe_3O_4 + CO \rightleftarrows 3FeO + CO_2 \quad (1)$$
$$FeO + CO \rightleftarrows Fe + CO_2 \quad (2)$$

within the range of temperature of 350° to 900° C. The next series of investigations was made by R. Schenck and his co-workers,[2] who sought to check the results of Baur and Glaessner's work within the range of 550° to 700° C. and to elucidate the conditions of formation of iron carbide. The equilibrium conditions at the higher temperatures, however, are generally understood to be much more complicated, owing chiefly to the formation of solid solutions between iron, its oxides, and carbide; nevertheless their determination is of much more practical importance than those at the lower temperatures.

It is well known that each of the reactions is reversible; equilibrium is established when the partial pressure of oxygen in the gaseous phase has become equal to the dissociation pressure of magnetic oxide in equation 1 and that of ferrous oxide in equation 2. These equilibria are subsequently designated by "the Fe_3O_4-FeO equilibrium" and "the FeO-Fe equilibrium," respectively.

As the Fe_3O_4-FeO equilibrium has three phases with three components, it must be bivariant. But the reaction involves no pressure change in the gaseous phase, hence the final composition of the latter is practically unaffected by pressure. To know the equilibrium conditions, the compositions of the gaseous phase at different temperatures must be determined. At the higher temperature, however, iron and its oxides dissolve one another in various proportions forming solid solutions; in many cases the content of oxygen in the solid phase becomes a new independent variable.

---

* Assistant Professor of Chemistry, Kioto Imperial University.

[1] *Zeit. phys. Chem.* (1903) **42**, 354. [2] *Ber.* (1905) **38**, 2132; (1907) **40**, 1704.

If a solid phase containing an excess of free carbon is subjected to a certain temperature in vacuo, an equilibrium is established when each of the reactions

$$Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2$$

and

$$2CO \rightleftharpoons C + CO_2 \qquad (3)$$

has acquired equilibrium at that temperature. The equilibrium condition may be made evident by measuring the pressure and composition of the resulting gaseous phase; but this method is available only for temperatures lower than about 700° C. Because the equilibrium pressure increases rapidly with increase of temperature, a temperature is soon reached at which the pressure is so great that a special apparatus is required.

It is necessary, therefore, to determine the conditions governing the formation of solid solutions, employing oxides or oxide mixtures, of various average oxygen content, as the solid phases, and CO or CO_2 content, as the initial gaseous phases, and then to find the equilibrium conditions of the reactions (1) and (2) when the solid phases are in proper composition showing no objectionable phenomenon of the formation of solid solution.

Experiments

Materials Used

Ferric oxide was prepared from carefully purified hydroxide. Ignition of the hydroxide at too high temperatures spoils the preparation: the oxide tends to become sintered, and, as may be judged from the dark reddish brown color, the resultant oxide is contaminated with lower oxides, formed at high temperatures, which to some extent remain unchanged at lower temperatures because of rapid cooling. Rather low temperatures were therefore used for the ignition and the fine powder was cooled slowly in a current of oxygen.

Metallic iron was prepared by heating its oxalate in a stream of hydrogen at about 600° C. Samples of the reduced commercial iron containing but a small amount of uncombined silica, but with no trace of manganese, were also used.

Carbon dioxide was produced by the action of dilute sulfuric acid on sodium bicarbonate suspended in water and was subsequently dried by passing it through concentrated sulfuric acid and phosphoric oxide.

Carbon monoxide was prepared by the action of concentrated sulfuric acid on oxalic acid; traces of oxygen were removed by heating it over yellow phosphorus, and other impurities were removed by passing it through a series of towers of concentrated caustic potash solution with and without pyrogallol, then through concentrated sulfuric acid; it was finally dried over phosphoric oxide.

Arrangement of Apparatus

The apparatus is diagrammatically represented in Fig. 1. A porcelain tube v, 2.3 cm. inside diameter and 40 cm. long, closed at one end and glazed both inside and out, in which a small kaolin plate supports a small magnesia boat of known weight and containing a weighed amount of iron oxide, was inserted into an ordinary Heraeus' furnace f in such a position that the boat was in the middle of the furnace and the open end of the vessel projected about 11 cm. A glass cup g was sealed to this end by Canada balsam that had been freed from easily volatile substances. During the experiments, the outside of this portion was cooled by circulating water.

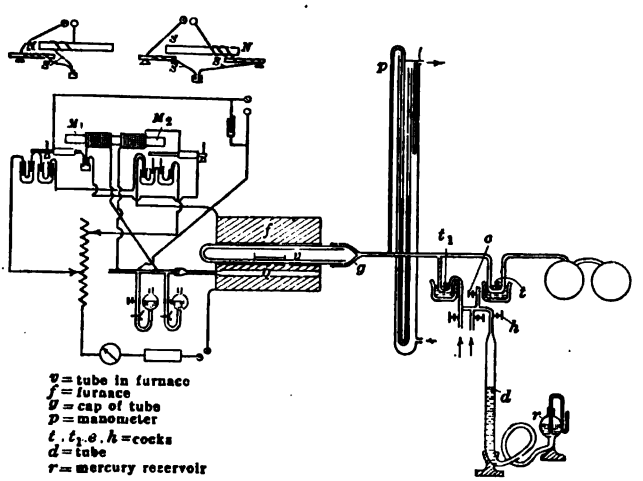

FIG. 1.—APPARATUS USED IN EXPERIMENTS.

The thermojunction of a Le Chatelier pyrometer, which was standardized against five metals, rested at the middle of the furnace and was in contact with the outside of the tube v. The end of the thermojunction was connected with a Siemens-Halske millivoltmeter graduated for each 10° C. Correction of temperature in the furnace was made by repeating Boudouard's experiment[3] and by determining the composition of the gaseous phase in equilibrium with amorphous carbon at various temperatures, at nearly one atmosphere, and then determining the average temperatures in the furnace by the result of Boudouard.

The glass cup g was connected with a Gaede molecular vacuum pump by a capillary glass tube having a cock t. One of the two capillary branches of the capillary tube was connected with a manometer p, and

[3] *Ann. chim. et phys.* (1901) **7**, 24, 5.

the other was fitted with the cock t_1 that controlled the passage of the gases. The manometer p consisted simply of a U-shaped capillary tube 80 cm. in height, the lower halves of which were filled with mercury, dipping vertically into a large glass tube through which a stream of water was allowed to flow slowly upwards. One arm of the U-tube was sealed, leaving a space filled with dry air, while the other was connected with the tube v by a capillary tube. The gas introduced in the porcelain tube v was once taken into an eudiometer d; it could also have been charged directly from the generators. A special device, shown at the left of Fig. 1, made it possible to maintain the temperature of the furnace constant within the range of 5° at 950° C. and 3° at 750° C.

Manipulation

After a weighed amount of ferric oxide was charged into the boat, the end of the porcelain tube v was sealed with the glass cup g, cocks t_1 and e being left open; cock h was opened and the eudiometer was filled with mercury, after which cocks h and e were closed and the whole system was evacuated. Cocks t and t_1 were then closed and the temperature of the furnace was raised to 400° or 500° C., where it was kept for about 2 hr.; any gas evolved was pumped off. The temperature was then increased, the gas to be charged was brought into the tube d and cocks t_1 and h opened; the gas was forced into the reaction vessel by raising the mercury reservoir r until the desired pressure was reached, when the cocks were closed and the reaction was allowed to proceed. To establish equilibrium properly requires roughly 2 hr. at 1100° C. and 14 to 20 hr. at 850° C. After the required length of time, the gas was drawn into the eudiometer and analyzed for carbonic acid, carbon monoxide, and, if necessary, nitrogen. From the result of the analysis, the actual volume of carbon monoxide that had entered the reaction could be calculated; this gave the weight percentage of oxygen in the solid phase, which stood in equilibrium with the gas phase.

After the repetition of these determinations, the boat was removed from the porcelain tube and weighed, so as to check the percentage of oxygen remaining in the solid phase. This percentage did not differ considerably from the calculated value and was taken as the correct number. Another check was made by direct analysis of the solid phase according to Margueritte's method, using Newth's apparatus, modified to introduce sulfuric acid into the flask without opening it. Samples containing metallic iron were determined, first, according to Milner-Merk's method[4] and then the amount of ferrous and total iron were determined as usual.

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[4] *Zeit. anal. chem.* (1902) **41**, 710.

Results of Experiment

The results are graphically represented in Figs. 2, 3, and 4. All the curves are first parallel with the abscissa, rise suddenly, become more

TABLE 1.—*Experiment Series* 1

(*Temperature*, 1070° *C.* *Initial solid phase*, 5.3946 *gm.* Fe_2O_3)

No.	Gaseous Phase				Solid Phase						
	Equil. Comp., Per Cent. CO	CO Charged		CO Entering the Reaction, c.c. (N.T.P.)	Oxygen Removed from Solid Phase (Cal.), gm.	Oxygen Remaining, gm.		Total Weight, gm.		Per Cent. O	
		Temp., ° C.	Vol., c.c.			Calculated	Found	Calculated	Found	Calculated	Found
1	0	21	84.58	78.54	0.05608	1.5648		5.3378		29.32	
2	0	22	94.40	87.37	0.06238	1.5024		5.2754		28.48	
3	0	21	88.00	81.74	0.05834	1.4441	1.4430	5.2171	5.2160	27.68	27.66
4	5.10	20	74.75	66.10	0.04719	1.3958		5.1688		27.00	
5	15.58	21	74.04	58.04	0.04144	1.3544		5.1274		26.41	
6	14.61	21	73.12	57.08	0.04140	1.3130	1.3603	5.0860	5.7333	25.82	26.50
7	13.37	21	71.55	57.56	0.04110	1.0755		4.1723		25.78	
8	14.36	21	75.95	60.40	0.04312	1.0324		4.1292		25.00	
9	24.55	21	75.95	53.21	0.03799	0.9944		4.0912		24.31	
10	29.50	20	75.95	23.80	0.01699	0.9774		4.0742		23.99	
11	38.17	20	75.90	17.84	0.01274	0.9647	0.9720	4.0615	4.0688	23.75	23.89
12	54.40	20	66.47	28.24	0.02016	0.8111		3.4597		23.44	
13	61.50	20	66.61	11.57	0.00826	0.8028		3.4514		23.26	
14	72.75	20	69.12	7.03	0.00502	0.7978	0.8013	3.4464	3.4499	23.15	23.23
15	72.25	20	70.60	18.25	0.01303	0.7087		3.0939		22.90	
16	72.45	20	70.60	10.21	0.00729	0.7014		3.0866		22.72	
17	71.05	20	70.34	18.97	0.01355	0.6879		3.0731		22.38	
18	72.42	20	72.16	18.54	0.01324	0.6747		3.0599		22.05	
19	72.59	20	73.96	18.89	0.01349	0.6612	0.6552	3.0464	3.0404	21.70	21.55
20	72.13	20	75.19	19.53	0.01394	0.5902		2.7893		21.16	
21	72.51	20	75.56	19.35	0.01382	0.5764		2.7755		20.77	
22	72.33	20	74.95	19.32	0.01379	0.5626		2.7617		20.37	
23	72.89	20	94.46	23.86	0.01704	0.5456	0.5414	2.7447	2.7405	19.88	19.76
24	72.06	20	73.77	19.20	0.01371	0.4728		2.4482		19.31	
25	72.00	20	74.07	19.32	0.01379	0.4590		2.4344		18.85	
26	72.95	20	72.49	18.27	0.01304	0.4460		2.4214		18.42	
27	72.30	20	84.82	21.90	0.01564	0.4304		2.4058		17.89	
28	72.57	20	81.44	20.82	0.01487	0.4155		2.3909		17.38	
29	72.78	20	93.67	23.76	0.01696	0.3985		2.3739		16.79	
30	72.41	20	97.10	24.96	0.01782	0.3807		2.3561		16.16	
31	72.98	20	72.20	18.18	0.01298	0.3275		2.0941		15.64	
32	72.38	21	71.31	18.29	0.01306	0.3144		2.0810		15.11	
33	73.01	21	99.27	24.87	0.01776	0.2966		2.0632		14.38	
43	85.60?						0.0698		1.8032		3.87
44	79.43	22	67.78	13.94	0.00995	0.0383		1.2376		3.10	
45	82.10	22	68.46	12.25	0.00875	0.0296		1.2289		2.41	
46	86.22	21	67.37	9.28	0.00663	0.0229	0.0224	1.2223	1.2217	1.88	1.83
47	88.07	21	67.26	8.02	0.00573	0.0167		1.2160		1.37	
48	90.66	21	68.53	6.40	0.00457	0.0121		1.2114		1.00	

At this point, the apparatus was damaged and the solid phase was oxidised in some degree.

49	90.91	21					0.0116		1.2109		0.95
54	95.43						0.0080		1.2073		0.66

TABLE 2.—*Experiment Series* 2

(*Temperature*, 1175° *C.* *Initial solid phase*, 4.3539 *gm.* Fe_2O_3)

No.	Equilibrium Composition of		No.	Equilibrium Composition of	
	Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O		Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O
1	0.37	29.36	5	15.36	26.37
2	0.46	28.63	6	14.95	25.59
3	0.60	27.89	7	17.04	24.79
4	15.53	27.14	At this point, the apparatus was damaged.		

TABLE 3.—*Experiment Series* 3

(*Temperature*, 1175° *C.* *Initial solid phase*, 1.3271 *gm.* Fe_2O_3)

No.	Equilibrium Composition of		No.	Equilibrium Composition of	
	Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O		Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O
1	0.67	27.68	33	94.75	1.58
2	15.14	25.51	34	95.70	1.37
3	32.60	23.54	35	96.64	1.21
4	65.08	22.72	36	96.43	1.03
5	75.62	22.03	37	96.66	0.87
6	75.21	21.32	38	95.61	0.66?
7	75.84	20.57	39	97.09	?
9	75.00	19.05	40	97.39	?
11	75.53	17.45	41	96.83	?
17	75.71	12.27	42	97.10	?
21	76.35	8.41	43	97.93	?
24	80.87	5.87	44	97.61	0.79[a]
25	81.13	5.08	45	96.53	?
26	82.32	4.27	46	94.74	?
27	87.04	3.71	48	95.93	?
28	89.93	3.18	49	96.25	?
29	91.10	2.78	50	96.37	?
30	91.94	2.43	51	95.77	?
31	93.50	2.09	54	96.72	?
32	94.46	1.83	56	97.03	?

[a]Calculated from the weight.

or less horizontal, rise, again become horizontal, and then rise gradually. Each of the lowest horizontals corresponds to a practically irreversible reaction

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \qquad (4)$$

At this period, the dissociation pressure of Fe_2O_3 containing Fe_3O_4 as solid

TABLE 4.—*Experiment Series* 4

(*Temperature*, 863° C. *Initial solid phase*, 3.7774 gm. Fe_2O_3)

No	Equilibrium Composition of		No.	Equilibrium Composition of	
	Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O		Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O
1	1.40	29.09	14	68.25	15.64
2	0.97	28.09	15	70.92	13.67
3	24.52	27.33	16	67.80	11.37
4	26.02	26.56	17	78.54?	9.75
5	25.18	25.82	18	70.89	7.44
6	25.71	25.00	19	84.93?	6.21
7	31.45	24.24	20	74.89	4.02
8	52.58	23.71	21	84.88	2.70
9	63.92	23.31	22	81.22	0.99?
10	67.48	22.95	23	80.00	?
11	67.40	22.58	24	89.66	?
12	65.47	19.75	25	86.39	?
13	67.89	17.73			

solution is so great that it does not permit the existence of carbon monoxide in the gaseous phase. From the data given by R. B. Sosman and J. C. Hostetter[5] concerning the dissociation pressure of the solid solution

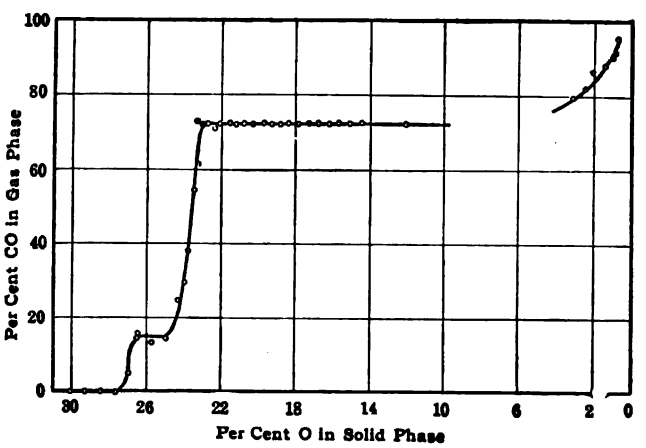


FIG. 2.—EXPERIMENT SERIES 1. TEMPERATURE 1070° C.

of Fe_3O_4 and Fe_2O_3 and the approximate formula of Nernst for the dissociation of CO_2

$$\log \frac{[CO]\cdot[O_2]^{1/2}}{[CO_2]} = -\frac{14{,}753.8}{T} + 1.221 \log T - 0.00037\,T + 1.3016 \quad (5)$$

[5] *Jnl.* Am. Chem. Soc. (1916) **38**, 807.

we find that until the percentage of oxygen in the solid phase decreased to about 28.12, the above chemical reaction should be practically irreversible and the measurement of the dissociation pressure in the iron-oxygen

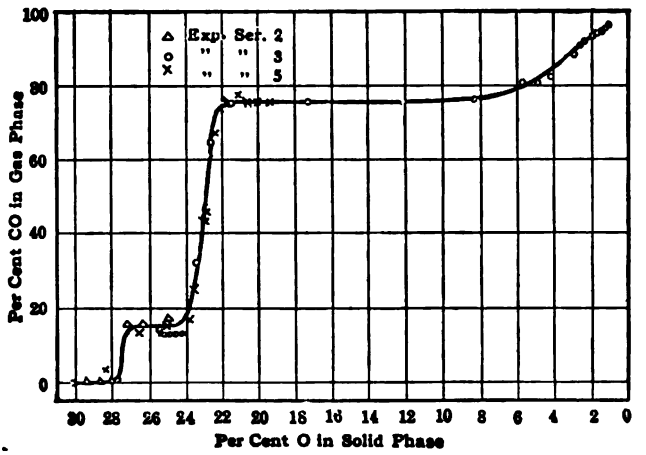


FIG. 3.—EXPERIMENT SERIES 2, 3 AND 5. TEMPERATURE 1175° C.

system by this method is impossible at 1100°C. and in the neighborhood of atmospheric pressure.

Figs. 2, 3, and 4 show a measurable carbon monoxide percentage when the percentage of oxygen in the solid phase has fallen to about 27.5, 27.6, and 28.0, respectively, at 1175°, 1070°, and 863°.

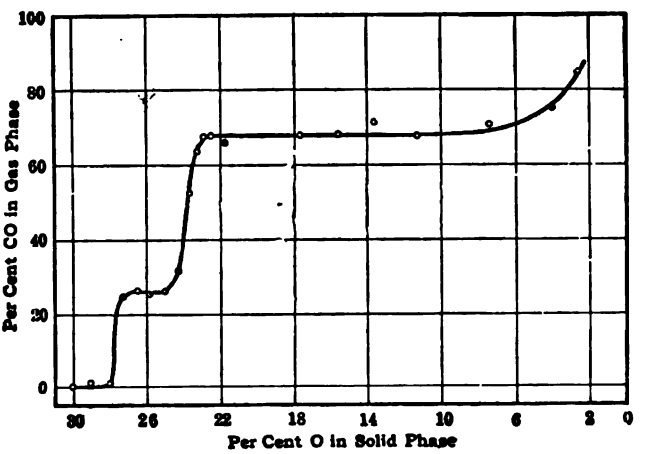


FIG. 4.—EXPERIMENT SERIES 4. TEMPERATURE 863° C.

As the percentage of oxygen decreases, the percentage of carbon monoxide rapidly increases; this upward sloping curve represents a condition in which the solid evidently consists of a single phase. When the oxygen content has been slightly lowered from this limit the curve

again becomes horizontal, indicating that the solid consists of two phases and that the new phase must be FeO, with which the solid has become saturated at the transition point from the sloping to the horizontal portion of the curve. The end of this horizontal portion indicates the disappearance of Fe_3O_4 as a distinct phase; the solid phase is now a saturated solution of Fe_3O_4 in FeO. The next almost vertical portion of the curve represents the gradual decomposition of Fe_3O_4 and the subsequent production of Fe, first dissolved in FeO and then appearing as a separate phase at the transition point of the steep slope to the new horizontal. The last change in direction of the curve indicates the transition from a bivariant to a trivariant system; FeO has disappeared as a separate phase and the solid has become a saturated solution of FeO in Fe. The uppermost slope of the curve represents the equilibrium condition of the new trivariant system in which the unsaturated solution of FeO in Fe is the solid phase.

Reversibility of Reactions

In order to make sure of the reversibility of the reactions, the following experiments were made:

Experiment Series 5.—Starting from a solid phase composed of pure Fe_2O_3, the system was brought up to the FeO-Fe horizontal portion of the curve by reduction, when it was oxidized by successive charges of CO_2 at 1175° C. Fig. 3 shows that the reactions in both directions give practically identical results. The small deviations at the transition points of the horizontals to the slopes may be ascribed to lack of time necessary to ensure the complete equilibrium.

Experiment Series 6.—A solid phase whose oxygen content corresponded with the FeO-Fe horizontal of the equilibrium curve at certain temperatures was subjected to the action of CO_2 and then to that of CO. The results are given in Table 5.

TABLE 5.—*Experiment Series* 6

(*Initial solid phase*, 7.1679 *gm. of oxides*)

No.	Temperature, Degrees C.	Equilibrium Composition of Gas Phase (Per Cent. CO)	
		Charged With CO_2	Charged With CO
1	1078	72.42	72.40[a]
2	1075	72.35[a]	
3	963	68.90	69.15
4	863	66.14	[b]
5	720	60.66	60.60

[a] Averages of three determinations. [b] See experiment series 4.

Experiment Series 7.—Similar experiments were made at the Fe_3O_4-FeO horizontal of the equilibrium curves; the results are given in Table 6

TABLE 6.—*Experiment Series* 7

(*Initial solid phase*, 1.6437 *gm. of oxides containing* 24.81 *per cent. oxygen*)

No.	Temperature, Degrees C.	Charged With	Equilibrium Composition of	
			Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O
1	1070	CO_2	16.42	25.27
2	963	CO_2	20.40	25.65
3	863	CO_2	25.49	26.27
4	627	CO	43.40	27.61[a]
5	627	CO	43.60	?[a]

[a] Vigorous gas absorption occurred.

So far as may be seen, there can be no doubt that the reactions are reversible.

Summary of Results

The data in Table 7 were obtained from the results of the experiments described. These data are plotted in two curves in Fig. 5, the coördi-

TABLE 7.—*Summary of Results*

Temperature, Degrees C.	Data Obtained From	Equilibrium Composition of Gas Phase, Per Cent. CO in	
		Fe_3O_4-FeO Equilibrium	FeO-Fe Equilibrium
1175	Fig. 3	15.2	75.5
1078	Experiment series 6		72.4
1075	Experiment series 6		72.3
1070	Experiment series 7	16.4	
1070	Fig. 2	15.0	72.3
963	Experiment series 6 and 7	20.4	69.0
863	Experiment series 6 and 7	25.5	66.1
863	Fig. 4	25.5	67.5
720	Experiment series 6		60.6
627	Experiment series 7	43.5	

nates of which are temperature and gaseous composition (per cent. CO). This graph is subsequently designated as "the *t-x* diagram." The upper curve represents the FeO-Fe equilibrium, and the lower the Fe_3O_4-FeO equilibrium, hence these are afterwards termed the "FeO-Fe curve" and the "Fe_3O_4-FeO curve" respectively.

The FeO-Fe curve, determined by Schenck and his collaborators at temperatures lower than those used by the author, seems to fit in well with the one given here. On the other hand, the author's experiments indicate that the minimum point seen in Baur and Glaessner's curve is not likely to exist, which opinion Schenck also has expressed.

Baur and Glaessner's Fe_3O_4-FeO curve is correct, due, perhaps, to a suitable selection of charging gas in their experiment, on the one hand,

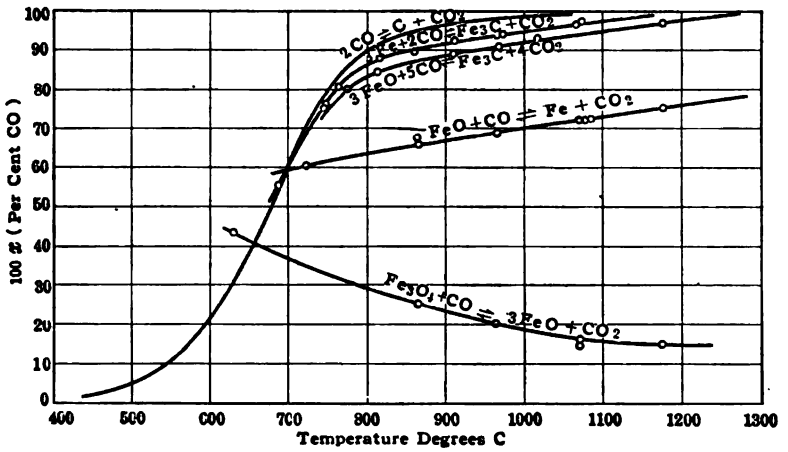


FIG. 5.—t-x DIAGRAM. PRESSURE, 1 ATMOSPHERE.

and to the suitable composition and amount of the initial solid phase on the other. The Fe_3O_4-FeO horizontal portions, as shown in Figs. 2, 3, and 4, are comparatively short, hence the employment of CO as the charging gas especially on a small amount of solid phase would easily introduce serious errors in the result.

By graphical interpolation, the following may be taken as the correct numbers used in later calculations:

Temperature, Degrees C	Equilibrium Composition of Gas Phase, Per Cent. CO in	
	Fe_3O_4-FeO Equilibrium	FeO-Fe Equilibrium
561		53.6[a]
627	43.5	57.0
662	39.7	58.4[a]
720	35.2	60.7
863	25.5	65.9
963	20.4	69.2
1070	16.4	72.4
1175	15.2	75.5

[a] These two figures are those determined by Schenck and his collaborators.

Equilibrium System Containing Free Carbon

Let K = equilibrium constant of reaction 3, and x = equilibrium composition of gas phase defined by the equation

$$\text{Per cent. CO} = 100x$$

then

$$K \times \frac{1-x}{x^2} = P \qquad (6)$$

where P = total pressure of system.

According to H. v. Juptner,[6]

$$\log K = 13.68 + 0.001081T - \frac{9037.34}{T} - 1.88 \log T \qquad (7)$$

where T denotes absolute temperature.

Substituting the experimental values of x and the calculated values of K in the left side of equation 6, we obtain the values of equilibrium pressure found in Tables 8 and 9.

Table 8.—*Values for FeO-Fe Equilibrium*

Temperature		x	Log K	Log P	P
Degrees C.	Degrees T.				
561	834	0.536	$\bar{2}.2530$	$\bar{2}.4618$	0.029
662	935	0.584	$\bar{1}.4400$	$\bar{1}.5263$	0.336
720	993	0.607	0.0181	0.0461	1.112
863	1136	0.659	1.2085	1.1035	12.7
963	1236	0.692	1.8914	1.6997	50.1
1070	1343	0.724	2.5218	2.2432	175.0
1175	1448	0.755	3.0618	2.6999	501.0

Table 9.—*Values for Fe_3O_4-FeO Equilibrium*

Temperature		x	Log K	Log P	P
Degrees C.	Degrees T.				
627	900	0.435	$\bar{1}.0574$	$\bar{1}.5325$	0.341
720	993	0.352	0.0181	0.7366	5.453
863	1,136	0.255	1.2085	2.3763	236.8
963	1,236	0.204	1.8914	3.1730	1,489.0
1,070	1,343	0.164	2.5218	4.0143	10,335.0
1,175	1,448	0.152	3.0618	4.6265	42,320.0

These values of P represent the equilibrium pressure of the system containing amorphous carbon.

[6] *Das Chem. Gleichgewicht* (1910) 243.

Dissociation Pressure of FeO and Fe_3O_4

Dissociation of FeO

The dissociation of FeO may be expressed by the reaction

$$FeO \rightleftarrows Fe + \tfrac{1}{2}O_2 \tag{8}$$

and that of CO_2 by

$$CO_2 \rightleftarrows CO + \tfrac{1}{2}O_2 \tag{9}$$

Equilibrium is established when the oxygen pressure of FeO becomes equal to that of the gaseous phase. From equation 5,

$$\log [O_2] = -\frac{29{,}507.6}{T} + 2.442 \log T - 0.00074T + 2.6032 - 2 \log \frac{[CO]}{[CO_2]} \tag{10}$$

Then,

T	x	$[O_2]$	T	x	$[O_2]$
834	0.536	5.41×10^{-27}	1236	0.692	4.60×10^{-16}
935	0.584	2.05×10^{-23}	1343	0.724	2.75×10^{-15}
993	0.607	7.06×10^{-21}	1448	0.755	7.84×10^{-15}
1136	0.659	4.75×10^{-18}			

These data may be represented well by the equation

$$\log [O_2] = -\frac{28{,}752}{T} - 1.79 \log T + 13.427 \tag{11}$$

Comparing the values of log $[O_2]$ calculated from this equation with those measured:

T	Log $[O_2]$ Calculated	Log $[O_2]$ Measured	Difference
834	−26.2767	−26.2667	+0.0100
935	−22.6415	−22.6876	−0.0461
993	−20.8922	−20.9063	−0.0141
1136	−17.3520	−17.3235	+0.0285
1236	−15.3698	−15.3373	+0.0325
1343	−13.5811	−13.5609	+0.0202
1448	−12.0872	−12.1055	−0.0183

Finally, for the dissociation pressure of FeO calculated from equation 11:

T	(O_2)	T	(O_2)
800	1.95×10^{-28}	1800	4.23×10^{-9}
1000	2.02×10^{-21}	2000	1.39×10^{-7}
1200	9.02×10^{-17}	2200	2.37×10^{-6}
1400	1.81×10^{-13}	2400	2.49×10^{-5}
1600	5.27×10^{-11}		

These values must be somewhat smaller than true ones, because the measurements in reality were concerned with the dissociation of FeO saturated with Fe.

Dissociation of Fe_3O_4

By calculation in the same manner as with FeO, for the dissociation pressure of Fe_3O_4

T	x	$[O_2]$	T	x	$[O_2]$
900	0.435	3.91×10^{-24}	1236	0.204	3.54×10^{-14}
993	0.352	1.00×10^{-20}	1343	0.164	4.92×10^{-13}
1136	0.255	1.94×10^{-16}	1448	0.152	2.32×10^{-10}

These data may be represented by the equation

$$\log [O_2] = \frac{32{,}254}{T} + 1.75 \log T + 7.23485 \qquad (12)$$

Comparing the values of $\log [O_2]$ calculated from this equation with those measured, gives the following:

T	Log $[O_2]$ Calculated	Log $[O_2]$ Measured	Difference
900	−23.4341	−23.4077	+0.0264
993	−20.0019	−19.9986	+0.0033
1136	−15.8108	−15.7112	+0.0996
1236	−13.4496	−13.4516	−0.0020
1343	−11.3074	−11.3085	−0.0011
1448	− 9.5086	− 9.6348	−0.1262

Calculating the dissociation pressure from this equation gives the following:

T	$[O_2]$	T	$[O_2]$	T	$[O_2]$
800	9.95×10^{-29}	1400	5.03×10^{-11}	2000	7.67×10^{-4}
1000	1.70×10^{-20}	1600	4.82×10^{-8}	2200	2.65×10^{-3}
1200	6.03×10^{-15}	1800	1.03×10^{-6}	2400	5.14×10^{-1}

It must be remembered that Fe_3O_4 was saturated with FeO in these experiments.

Equilibrium System of Iron with or without Oxygen, Carburized Iron and Gas Consisting of Carbon Monoxide or Carbon Dioxide or Both

General Method of Investigation

A solid phase, consisting of a solid solution of FeO in Fe, and a gas phase, consisting of CO and CO_2, form a trivariant system in which the final composition of the gas phase is practically independent of the pressure of the system. But if the amount of oxygen in the solid phase is decreased to a very small quantity by successive reduction with CO, a new chemical reaction begins, as shown by the decrease of pressure in the system when the reaction vessel is charged with fresh CO. Although the original pressure is soon recovered, in the case of a solid phase insufficiently reduced, the recovery is slower after each experiment. When

the pressure ceases to be recovered, equilibria are established under reduced pressures.

Under such conditions of solid phase, the composition of the gaseous phase that stands in equilibrium with the solid tends to show some irregularity: the percentage of CO in the total amount of CO and CO_2 is sometimes decreased and sometimes increased according to the magnitude of the final pressure in the equilibrium system. But, when the pressure is practically the same, the composition of the gas phase seems to be practically constant. The latter fact was shown in the third experiment series, in which the final composition of the gas is practically 97 per cent CO, since the final pressures were nearly one atmosphere.

If the solid phase is examined under this condition, it is apparent that carburization has taken place and that the solid phase contains, besides oxygen, some combined carbon.

The reaction of carburization may be considered to occur according to either of the following equations, which have been proposed by many authors

$$3Fe + 2CO \rightleftarrows Fe_3C + CO_2 \tag{13}$$

$$3FeO + 5CO \rightleftarrows Fe_3C + 4CO_2 \tag{14}$$

If K_1 and K_2 are the equilibrium constants of these reactions,

$$K_1 = \frac{[CO]^2}{[CO_2]} = \frac{x^2}{1-x} \times P \tag{15}$$

$$K_2 = \frac{[CO]^5}{[CO_2]^4} = \frac{x^5}{(1-x)^4} \times P \tag{16}$$

If either K_1 or K_2 is constant for various values of P and x, the corresponding carburizing reaction should be the probable one to occur in the system. As long as no better explanation of the phenomena is given, it is reasonable to believe that the reaction coincides with that equation, at least in its final result, no matter how complex the intermediate reactions may be.

Experiments

The arrangement of apparatus and the manipulations were the same as in the previous experiments, except that the final pressures were carefully registered in each case. The establishment of equilibrium was ensured by watching the manometer, as the pressure ceases to change when equilibrium is attained.

Interpretation of Results

After experiment 11, the percentage of CO in the gas phase, instead of rising gradually in each experiment, became practically constant (about 91 per cent.) when the pressure was approximately one atmos-

TABLE 10.—*Experiment Series* 8

(*Initial solid phase, 7.7344 gm. of reduced iron containing* 2.01 *per cent. of oxygen, but no trace of manganese. Charging gas,* CO)

No.	Temperature, Degrees C.	Equilibrium Condition in Gaseous Phase		Per Cent. O in Solid Phase, Calculated
		Pressure, Atmospheres	Per Cent. CO	
1	965	1.0778	70.72	1.81
2	965		72.27	1.60
3	965		75.20	1.43
4	965		78.92	1.27
5	965		82.28	1.13
6	965		83.87	1.01
7	965		85.04	0.90
8	965		87.23	0.79
9	965		88.50	0.71
10	965		88.79	0.62
11	965	0.9785	91.14	0.57
12	965	0.8893	91.27	
13	965	0.9665	90.73	
14	965	0.6159	91.65	
15	965	0.9941	90.81	
16	965	0.3176	93.78	
17	965	0.5327	92.20	
18	965	1.0270	91.22	
19	743	0.7710	79.46	
20	743	0.9334	76.84	
21	857	1.0253	86.27	
22	857	1.0107	87.12	
23	857	0.9973	87.25	
24	1070	1.1284	96.87	
25	1070	0.9783	97.39	
26	968	0.9727	94.41	
27	968	1.0221	93.77	
28	744	0.8908	77.67	
29	857	1.0058	89.05	
30	857	0.9905	89.89	
31	857	0.9148	90.29	
32	761	0.9272	81.77	
33	814	1.0668	85.18	
34	814	0.9006	88.08	
35	814	0.9487	87.69	
36	814	0.8729	89.33	
37	814	0.8783	89.25	
38	963			
39	963			
40	963			
41	963	0.9487	98.54	
42	963	0.9506	98.03	
43	963	0.9550	97.92	
44	686	1.0096	57.51	
45	814	0.9169	86.60	
46	814	0.8931	88.22	

NOTE.—Experiments 1 to 3 of experiment series 8 were reductions accompanying no pressure change; at the beginning of experiment 4, some decrease in pressure was noticed. The amount of this decrease gradually became larger, but, until experiment 8, the reduced pressures nearly regained their initial magnitude although the recovery became more and more difficult. Pressure remained depressed in experiment 9 and afterwards.

An examination of the solid phase at the end of experiment 18 showed that strong carburization had taken place, but no sign of soot deposition was observed. Experiments 38 and 40 were made for the purpose of complete carburization of the solid phase.

phere, and it seemed to increase with decrease of pressure. The calculated values of K_1 and K_2 corresponding to 965° C. are as follows:

No.	P	x	Log K_1	Log K_2
16	0.3176	0.9378	0.6523	$\bar{4}$.1873
17	0.5327	0.9220	0.7639	$\bar{3}$.9818
14	0.6159	0.9165	0.7921	$\bar{3}$.9134
12	0.8893	0.9127	0.9087	$\bar{3}$.9367
13	0.9665	0.9073	0.9336	$\bar{3}$.9056
11	0.9785	0.9114	0.9626	$\bar{3}$.9994
15	0.9941	0.9081	0.9504	$\bar{3}$.9348
18	1.0270	0.9112	0.9883	$\bar{4}$.0381

Apparently there is a serious gradation in the column of log K_1; the numbers in the column of log K_2 agree well with one another. Therefore the reaction that took place during these experiments coincides with reaction 9, at least in its final result.

Iron carbide produced in this way might have dissolved to a certain extent in the pre-existing solid phase at the earlier stage, but at last the carbide or some other substance rich in carbon made its appearance as a separate solid phase. As a result, the equilibrium system must have changed to a divariant one.

The mean value of log K_2 is $\bar{3}$.987, from which equilibrium pressures corresponding to any desired value of x can be calculated, thus

x	P	x	P	x	P
0.1	6.36×10^{8}	0.8	4.74×10	0.95	0.079
0.2	1.24×10^{7}	0.9	1.644	0.96	0.030
0.3	9.59×10^{5}	0.91	1.021	0.97	0.009
0.4	1.23×10^{5}	0.92	0.603	0.98	0.002
0.5	1.94×10^{4}	0.93	0.335	0.99	0.0001
0.6	3.20×10^{3}	0.94	0.172	1.00	0.0
0.7	4.68×10^{2}				

By graphic interpolation, 0.9105 is found to be the value of x corresponding to $P = 1$. Consequently, at the temperature of 965° C. and under a pressure of one atmosphere, an equilibrium will be established when the gaseous composition becomes 91.05 per cent. CO.

The results of experiments 19 and 20 give

No.	P	x	Log K_2	Log K_1
19	0.7710	0.7946	2.1374	0.3748
20	0.9334	0.7684	1.9391	0.3765

This time log K_1 gives a more constant value than log K_2, showing that the reaction was either carburization, according to reaction 8, or soot deposition, in accordance with reaction 3. From the mean value of

log K_1, $x = 0.7549$ for $P = 1$. This equilibrium point deviates slightly from the carbon curve wrought out by Boudouard. Hence the equilibria should have been those of carburization.

Experiments 21 to 23 were made under the pressures of practically one atmosphere. The first result differs slightly from the following two: the gaseous composition acquired its constant value first in experiment 22. Hence the last two numbers are to be taken as those representing the true divariant equilibria at 857° C. The mean gaseous composition is 87.19 per cent. CO, but the nature of this reaction cannot be decided from these data. However, as shown in Fig. 6, this equilibrium point lies exactly on the equilibrium curve of reaction 9, which is afterwards

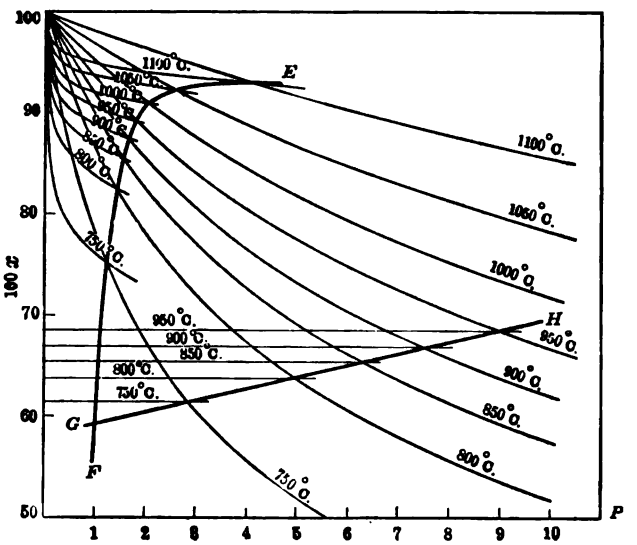


FIG. 6.—P-x DIAGRAM.

wrought out from other data. The solid phase must have been oxidized during the experiment at 743° C. because formerly it was so well reduced that its oxygen pressure admitted of carburization during the experiment at 965°, and the same solid phase is incapable of being carburized at 857° without previous reduction. It is also clear that the solid phase which stood in equilibrium of reaction at 965° was capable of being carburized according to reaction 9 at 743°.

Experiments 24 and 25 give the following results:

No.	P	x	Log K_2	Log K_1
24	1.1284	0.9687	6.0013	1.5293
25	0.9783	0.9739	6.2665	1.5509

The mean value of log K_1 is 1.540, which gives $x = 0.9727$ for $P = 1$. This equilibrium point deviates in a marked degree from the carbon curve

of Boudouard; therefore the reaction was that of carburization in accordance with reaction 8. It must be remembered that the solid phase was brought from 857° to 1070°. Perhaps the amount of charging gas was so large, compared to the amount of solid in experiment 24, that the former reduced the latter sufficiently to establish Fe-Fe_3C equilibrium at 1070°.

Experiments 26 and 27 give the following results.

No.	Log K_2	Log K_1
26	4.7534	1.1606
27	4.5521	1.1591

The mean value of log K_1 is 1.1599, which gives $x = 0.9390$ for $P=1$; this point is not on the carbon curve.

Experiment 28 gives $x = 0.7600$ for $P = 1$ if the reaction is assumed to be that of carburization; which is a reasonable assumption because the solid phase showed the carburization equilibrium of reaction 8 to be 980° in the previous experiment. The calculated equilibrium point agrees with the results of experiments 19 and 20.

Experiment 29 shows apparently a transitional equilibrium resulting from oxidation of the solid phase in the previous experiment at 744°. But the solid phase was well reduced and carburized at higher temperatures during experiments 24 to 27 and it was exposed to 744° in only one experiment. Therefore the result of oxidation was not so serious as in experiment 21. The mean value of log K_1, which is constant in experiments 30 and 31, is 0.8920; this gives $x = 0.8968$ for $P = 1$.

From experiment 32, $x = 0.8081$ for $P = 1$, on the assumption that log K_1 is a constant. This assumption is permissible because the solid phase is brought from 857° to 761°.

Experiments 33 to 37 furnish an interesting example of the transition of reactions.

No.	P	x	Log K_1
33	1.0668	0.8518	0.7179
34	0.9006	0.8808	0.7680
35	0.9487	0.8769	0.7728
36	0.8729	0.8933	0.8148
37	0.8783	0.8925	0.8135

The first is obviously a transitional equilibrium resulting from the oxidation of the solid phase in the previous experiment. The second and the third give one group of vicinal numbers as log K_1; they must correspond to the equilibrium of reaction 8. The mean value of log K_1 is 0.7704 from which $x = 0.8712$ for $P = 1$. The fourth and fifth experiments give another group of vicinal numbers as log K_1; this group corresponds to the reaction of soot deposition because the mean value of log K_1 is 0.8141, which gives $x = 0.8809$ for $P = 1$, which point lies exactly on the carbon curve of Boudouard. Hence it is known that the

solid phase, or at least its surface layer, was saturated with carbon at the beginning of experiment 36, and the equilibrium point had been displaced toward the carbon curve before the end of that experiment.

After the repeated carburization of the solid phase, experiments 41 to 43 were made to determine the position of the carbon curve at 963°. The calculated results are:

No.	P	x	Log K_1
41	0.9487	0.9854	1.8000
42	0.9506	0.9803	1.6663
43	0.9550	0.9792	1.6437

There is a gradation in the column of log K_1, but the absolute values are much larger than those corresponding to the equilibrium of Fe, Fe_3C, CO, and CO_2. This shows that only the surface layer had acquired the composition of pure cementite by the rapid reaction of fresh carbon monoxide during the previous carburizing operation. Hence, in experiment 41, the gaseous phase in equilibrium was so rich in CO that soot was deposited upon the cementite crust, because the calculated value of x corresponding to $P = 1$ is 0.9846, which is on the carbon curve. The next two equilibria seem to be transitional ones, the position of the equilibrium point depending entirely on the carbon content of the surface layer of solid phase.

The equilibrium pressure in experiment 44 was nearly one atmosphere and the equilibrium point lies nearly on the carbon curve.

Experiments 45 and 46 give the following results:

No.	P	x	Log K_1
45	0.9169	0.8660	0.7103
46	0.8931	0.8822	0.7709

Log K_1 in the second experiment exactly coincides with the equilibria of Fe, Fe_3C, CO, and CO_2 determined by experiments 34 and 35, hence the solid phase was again oxidized during the previous experiment at 686°. The equilibrium in the first experiment was only a transitional one.

This series of experiments shows:

1. The first period of carburizing reaction coincides, at least in its result, with

$$3FeO + 5CO \rightleftharpoons Fe_3C + 4CO_2 \qquad (14)$$

and at the later period with

$$3Fe + 2CO \rightleftharpoons Fe_3C + CO_2 \qquad (13)$$

2. There exist the transitional equilibria between the above two, between the first and FeO-Fe equilibrium, and between the second and carbon equilibrium.

3. Equilibria at lower temperatures occur with more oxidized form of solid phase than at the higher temperatures even in the same carburizing reaction.

Confirmatory Experiments

The following experiments were made as a check on the previous experiments on reaction 14 at various temperatures and under a pressure of practically one atmosphere. Account was taken of the variation in the composition of the solid phase: in most cases, a solid solution of FeO in Fe containing a large amount of oxygen was used as the initial solid phase. The equilibrium composition of gas phase, after successive experiments, became constant when the experiment at that temperature was finished. If the deviation of equilibrium pressure from one atmosphere was not negligible, the equilibrium constant was calculated and from this the gaseous composition corresponding to one atmosphere was obtained as usual.

TABLE 11.—*Experiment Series* 9

(*Temperature, 907° C. Initial solid phase, solid solution of FeO in Fe containing 2.01 per cent. oxygen. Charging gas, CO*)

No.	Equilibrium Conditions		Remarks
	Pressure, Atmospheres	Composition of Gas, Per Cent. CO	
1	1.1764	82.38	
2	0.9863	83.70	
3	1.0753	85.49	
4	1.0716	86.70	
5	1.0919	87.19	
6	1.1539	87.54	
7	0.9838	89.04	
8	0.9884	88.71	Average 89.15
9	0.9793	89.31	
10	0.9979	89.55	

TABLE 12.—*Experiment Series* 10

(*Temperature, 772° C. Initial solid phase, solid solution of FeO in Fe containing 2.01 per cent. oxygen. Charging gas, CO*)

No.	Equilibrium Conditions		Remarks
	Pressure, Atmospheres	Composition of Gas, Per Cent. CO	
1	0.8204	77.72	
2	1.0910	75.23	
3	0.9029	79.06	
4	0.9977	80.00	Average 80.22
5	1.0023	81.26	
6	0.9848	80.56	

TABLE 13.—*Experiment Series* 11

(*Temperature*, 810° *C. Initial solid phase, end product in experiment series* 10. *Charging gas, CO*)

No.	Equilibrium Conditions		Remarks
	Pressure, Atmospheres	Composition of Gas, Per Cent. CO	
1	1.0080	85.22	
2	0.9458	86.06	
Vessel was evacuated, filled with CO, closed, and allowed to stand for 1 hr., then evacuated. This process was repeated three times, when the reaction with CO was allowed to go on as before.			
3	0.9375	82.60	
4	0.9818	84.64	Average
5	1.0204	84.51	84.58

TABLE 14.—*Experiment Series* 12

(*Temperature*, 1014° *C. Initial solid phase, end product in experiment series* 17. *Charging gas, CO*)

No	Equilibrium Conditions	
	Pressure, Atmospheres	Composition of Gas, Per Cent. CO
1	1.0118	96.95
Solid phase was subjected to oxidizing action of CO_2 as in experiment series 11.		
2	0.9501	81.56
3		87.20
4	1.0181	88.79
5		
6		
7		
8	0.9843	92.18
9	0.9759	92.57
10	0.9799	92.82
11	0.9623	93.16
12	0.9601	93.20

The average value of log K_2 calculated from the last two results is 4.4943; this gives $x = 0.9312$ for $P = 1$.

This time log K_1 gave more constant values than log K_2; hence the conditions of equilibrium of reaction 9 have not been determined. From the last three data, $\bar{1}.852$ is the average value of log K_1, which gives $x = 0.5548$ for $P = 1$. This equilibrium point lies nearly on the carbon curve

TABLE 15.—*Experiment Series* 13

(*Temperature, 685° C. Initial solid phase, end product in experiment series* 12. *Charging gas, CO*)

No.	Equilibrium Conditions		Log K_1	Log K_2
	Pressure, Atmospheres	Composition of Gas, Per Cent CO		
1	0.6389?	61.73	$\bar{1}$.8036	0.4265
2	0.7086	56.43?	$\bar{1}$.7142	0.0512
3	0.4170	70.46	$\bar{1}$.8456	0.9782
4	0.6385	64.00	$\bar{1}$.8612	0.6109
5	0.4239	70.36	$\bar{1}$.8500	0.9764

of Boudouard; but as there was no sign of soot deposition in the solid phase or on the wall of the vessel, the reaction was presumably that of carburization.

The following experiments were made as a check for the equilibrium conditions of reaction 13, employing various forms of iron with no oxygen content as the initial solid phase.

Experiment Series 14.—No. 1. Temperature, 909° C. Initial solid phase, 7.0368 gm. of reduced iron. Charging gas, CO. Composition of gas in equilibrium, 92.97 per cent. CO. Equilibrium pressure, 0.9187 atmosphere. Calculated composition of gas corresponding to an equilibrium pressure of 1 atmosphere, 92.45 per cent. CO.

No. 2. Temperature, 963° C. Initial solid phase, 19.1430 gm. of white pig iron of the following composition: 3.708 per cent. C, 0.063 per cent. P, 0.028 per cent. S, 0.084 per cent. Si, trace of Mn. Charging gas, CO_2. Composition of gas in equilibrium, 91.18 per cent. CO. Equilibrium pressure, 1.5440 atmosphere. Calculated composition of gas corresponding to an equilibrium pressure of 1 atmosphere, 93.9 per cent. CO.

No. 3. Temperature, 1065° C. Initial solid phase, 5.1295 gm. fine piano wire. Charging gas, CO. Composition of gas in equilibrium: (*a*) 96.50 per cent. CO; (*b*) 96.64 per cent. CO. Equilibrium pressures: (*a*) 0.959 atmosphere; (*b*) 1.100 atmospheres. Calculated composition of gas corresponding to an equilibrium pressure of 1 atmosphere: (*a*) 96.35 per cent. CO; (*b*) 96.93 per cent. CO; mean 96.64 per cent. CO.

No. 4. Temperature, 968° C. Initial solid phase, 1.3938 gm. of reduced iron. Charging gas, mixture of CO and CO_2; CO in charging gas: (*a*) 100 per cent.; (*b*) 100.0 > < 95.6 per cent.; (*c*) 100.0 > < 94.74 per cent. Equilibrium pressures: (*a*) 0.9349 atmosphere; (*b*) 0.9232 atmosphere; (*c*) 0.9443 atmosphere. Calculated composition of gas corresponding to

an equilibrium pressure of 1 atmosphere: (*a*) 94.62 per cent. CO; (*b*) 94.74 per cent. CO; (*c*) 94.49 per cent. CO. From these data:

Experiment	Log K_1	$100x$ ($P = 1$)
a	1.1915	94.28
b	1.1974	94 35
c	1.1847	94.20
		94.28 average

TABLE 16.—*Equilibrium Points of Carburizing Reactions*

Experiment Series	Temperature, Degrees C.	$100x$ Corresponding to $P = 1$ in Equilibrium	
		$3Fe + 5CO \rightleftharpoons Fe_3C + 4CO_2$	$3FeO + 2CO \rightleftharpoons Fe_3C + CO_2$
13	685		55.48
8	743		75.49
8	744		76.00
8	761		80.81
10	772	80.22	
11	810	84.58	
8	814		88.09
8	857		89.68
9	907	89.15	
14	909		92.45
14	963		93.90
8	965	91.05	
8	968		93.90
14	968		94.28
12	1014	93.12	
14	1065		96.64
8	1070		97.27
3	1176	97	

Summary of Results

The equilibrium points of carburizing reactions may be summarized as shown in Table 16. These equilibrium points are plotted in two curves in Fig. 5. They are subsequently designated as "carburization curves" and to distinguish one from the other they are marked "Fe-Fe_3C cnrve" and "FeO-Fe_3C curve."

Influence of Pressure on Equilibria

The equilibrium constant at any required temperature in either of the two carburizing reactions can be calculated from the *t-x* diagram. Thus for the Fe-Fe_3C equilibrium:

Temperature, Degrees C.	x	Log K_1	Temperature, Degrees C.	x	Log K_1
1100	0.981	1.7046	900	0.917	1.0057
1050	0.967	1.4524	850	0.897	0.8927
1000	0.951	1.2662	800	0.866	0.7479
950	0.935	1.1287	750	0.783	0.4511

and for the FeO-Fe_3C equilibrium:

Temperature, Degrees C.	x	Log K_1	Temperature, Degrees C.	x	Log K_1
1200	0.977	6.5025	900	0.889	3.5632
1150	0.964	5.6952	850	0.868	3.2103
1100	0.950	5.0927	800	0.838	2.7781
1050	0.937	4.6613	750	0.762	1.9034
1000	0.922	4.2553	700	0.620	0.6428
950	0.906	3.8931			

TABLE 17.—*Value of P for Fe-Fe_3C Equilibrium*

	Temperature, in Degrees C.							
x	1100	1050	1000	950	900	850	800	750
	Equilibrium Pressures, in Atmospheres							
0.98	1.056	0.590	0.384	0.280	0.211	0.164	0.117	0.059
0.96	2.198	1.230	0.801	0.584	0.440	0.339	0.243	0.123
0.94	3.439	1.924	1.253	0.913	0.688	0.530	0.380	0.192
0.92	4.787	2.678	1.744	1.271	0.958	0.738	0.529	0.267
0.90	6.253	3.498	2.279	1.660	1.251	0.964	0.691	0.349
9.88	7.849	4.391	2.860	2.084	1.570	1.210	0.867	0.438
0.86	9.588	5.364	3.494	2.546	1.918	1.479	1.059	0.535
0.84	11.49	6.426	4.185	3.050	2.297	1.771	1.269	0.641
0.82		7.586	4.941	3.601	2.712	2.091	1.498	0.756
0.80		8.855	5.768	4.203	3.166	2.441	1.749	0.823
0.78		10.25	6.674	4.864	3.664	2.825	2.024	1.022
0.76			7.669	5.589	4.210	3.246	2.326	1.174
0.74			8.763	6.386	4.810	3.709	2.657	1.341
0.72			9.969	7.265	5.472	4.219	3.023	1.526
0.70			11.30	8.234	6.203	4.783	3.427	1.730
0.68				9.308	7.011	5.406	3.873	1.955
0.66				10.50	7.908	6.097	4.369	2.205
0.64					8.904	6.866	4.919	2.484
0.62					10.02	7.722	5.533	2.793
0.60						8.680	6.219	3.139
0.58						9.753	6.988	3.527
0.56						10.96	7.853	3.964
0.54							8.829	4.457
0.52							9.935	5.015
0.50							11.14	5.650

TABLE 18.—*Value of P for FeO-Fe$_3$C Equilibrium*

x	Temperature, in Degrees C.									
	1150	1100	1050	1000	950	900	850	800	750	700
	Equilibrium Pressures, in Atmospheres									
0.98	0.070	0.022								
0.96	1.556	0.389	0.144							
0.94	8.753	2.186	0.810	0.318	0.138					
0.92	30.8	7.693	2.849	1.119	0.486	0.227	0.101			
0.90		20.97	7.765	3.049	1.324	0.620	0 275	0.102		
0.88			18.02	7.073	3.072	1.437	0.638	0.236		
0.86				14.70	6.386	2.987	1.325	0.490	0.126	
0.84					12.25	5.732	2.543	0.940	0.227	
0.82						10.36	4.596	1.700	0.391	
0.80							7.925	2.929	0.650	
0.78							13.17	4.868	0.650	
0.76								7.851	1.048	
0.74								12.36	1.649	
0.72									2.543	
0.70									3.858	
0.68									5.774	
0.66									8.544	0.469
0.64									12.52	0.687

The equilibrium pressures corresponding to various values of x at various temperatures may be calculated from the constants just obtained. These equilibrium points are plotted in isothermals in Fig. 6, x and P being the coördinates; these curves are designated "*P-x* isothermals." To distinguish one from the other they are marked "Fe-Fe$_3$C isothermal" and "FeO-Fe$_3$C isothermal." "The FeO-Fe isothermals," which should be straight lines, are also represented.

The point of intersection of an Fe-Fe$_3$C isothermal with the corresponding FeO-Fe$_3$C isothermal is the point where the two kinds of carburization equilibria are established simultaneously, *i.e.*, carburization in Fe and FeO may be effected at the same time: these points are plotted in a curve *E-F*. The point of intersection of a FeO-Fe$_3$C isothermal with the corresponding FeO-Fe isothermal is the point where the reduction and carburization of FeO may be effected at the same time; these points are plotted in a curve *G-H*. The three kinds of equilibrium should be established simultaneously at the intersection of *E-F* and *G-H*, the coordinate of which point seems to be approximately $P = 1$ and $x = 0.59$. The disposition of the two carburization curves in the *t-x* diagram shows the same fact. The carbon curve of Boudouard on the same diagram should also pass through the same point because the FeO-Fe curve in the *t-x* diagram intersects with the carbon curve at the point $x = 0.593$ and $t = 695$. This at once shows that the four kinds of equilibrium, namely the carbon equilibrium, two carburization equilibria, and FeO-

Fe equilibrium, are established at the same time at a point $P = 1$, $x = 0.593$, and $t = 695°$ C.; and that both the carbon isothermal and Fe-Fe_3C isothermal in the P-x diagram coincide in their entire length with each other at 693° C.

Phenomena of Pressure Change during Carburization and Decarburization

If a current of CO is rapidly passed over crystals or fragments of crystals of the mineral magnetite at a temperature of about 800° to 1000° C.; or if a closed reaction vessel is used, if the charging and withdrawing of CO are rapidly repeated, the surface and fissures of the oxide are quickly reduced and carburized so that it becomes covered by thin crusts, the composition of which ranges from high-grade oxide, in the inner layer, to highly carburized iron in the outer layer. Even a rich deposition of soot upon the surface may be effected by a sufficiently rapid supply of fresh CO. But if the supply of CO is stopped and the whole system is allowed to stand with the reaction taking place in a confined space and kept at a definite temperature, the carbon content of the solid, phase is gradually oxidized by oxygen produced by dissociation of the solid and the pressure of the system is gradually increased. The following experiments show the manner of pressure-change with regard to time.

EXPERIMENT SERIES 15

No. 1. Temperature, 907° C. Initial solid phase, 17.7414 gm. of fragments of magnetite crystal not larger than grains of corn, surface being previously reduced and carburized. Initial gas phase, CO.

In the tables h is reading of mercury column in right side of capillary tube of manometer; t is time, in minutes; P is pressure, in atmospheric units.

t	h	P	t	h	P	t	h	P
0	467	1.3312	50	462		105	469	1.3344
2	460		55	463		110	469	
5	457		60	466		115	469	
10	455	1.2707	65	467		120	469	
15	455		70	467.5	1.3270	125	469	
20	455		75	467.5		130	469	
25	455		80	467.5		150	474	1.3606
30	455		85	467.5		165	474	
35	455.5		90	467.5		180	474	
40	459		95	467.5		190	474	
45	460		100	468		200	474	

A gas analysis at the end gave 79.01 per cent. CO.

No. 2. Temperature and initial conditions, same as in No. 1.

t	h	P	t	h	P	t	h	P
0	475	1.3691	45	468		90	475.6	
5	467		50	471		95	475.6	
10	466.5	1.3252	55	472.5		100	478.5	
15	466.5		60	473	1.3546	105	480	
20	466.5		65	473		110	481.5	
25	466.5		70	473		115	482.5	1.405
30	466.5		75	474		120	482.5	
35	467		80	474.4		150	482.5	
40	467.5		85	475.6	1.3601			

A gas analysis at the end gave 84.44 per cent. CO.

No. 3. Temperature, 853° C. Initial conditions, same as in No. 1.

t	h	P	t	h	P	t	h	P
0	443	1.2069	40	428		120	431	
2	433		50	428		130	432	1.1542
5	427	1.136L	60	428		140	432	
10	427		70	428		150	432	
15	427		80	430		160	432	
20	427		90	431	1.1481	170	432	
25	427		100	431				
30	428	1.1362	110	431				

A gas analysis at the end gave 76.70 per cent. CO.

These results are graphically represented in Figs. 7 and 8, which represent the same type of pressure change. First, the pressure falls with remarkable speed, then after remaining stationary for some time, it increases rapidly; after a second pause, it again increases; a third pause is succeeded by the third increase; after the fourth pause there is no further pressure change. Many similar experiments were made by the writer and graphs of similar type were always obtained.

The first horizontal seems to represent an equilibrium state of reaction 3. If the reaction starts from pure CO and if P_0 is the initial pressure of the system,

$$xP = P_0 - 2(P_0 - P) \tag{17}$$

where P = total pressure and x = gaseous composition as before.

The intersection of this hyperbola in the P-x plane with the carbon isothermal should be the point where an equilibrium is established between soot and the gaseous phase. Exactly the same statement holds true with the reaction

$$3Fe + 2CO \rightleftharpoons Fe_3C + CO_2$$

in which the point of intersection of the hyperbola with the Fe-Fe_3C isothermal is where the above equilibrium is actually established.

Fig. 5 shows that an equilibrium is established between carbon and its oxides at 907° C. when $x = 0.972$ and $P = 1$. This gives 33.742 as the equilibrium constant, from which $x = 0.9649$ when $P = 1.2707$ and $x = 0.9636$ when $P = 1.3252$. From equation 17,

$$P_0 = (2 - 0.9649) \times 1.2707 = 1.315, \text{ in experiment 1}$$
and $$P_0 = (2 - 0.9636) \times 1.3252 = 1.373, \text{ in experiment 2}$$

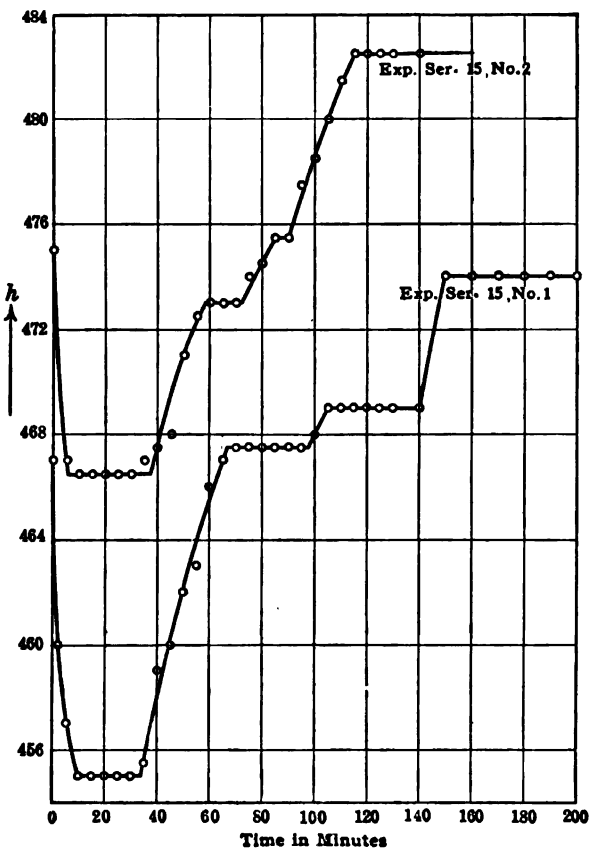


FIG. 7.—EXPERIMENT SERIES 15. TEMPERATURE 907° C.

These values of P_0 should be equal to the initial pressure in each experiment, respectively, if it is assumed that the first horizontals in Fig. 7 represent the equilibrium states of soot and gases. Comparing these values with those actually measured, it is found that their agreement is within the range of accuracy of the equilibrium constant.

No.	P_0 Calculated	P_0 Measured	Difference
1	1.315	1.331	−0.016
2	1.373	1.369	+0.004

As 0.918 is the value of x corresponding to the Fe-Fe_3C equilibrium at 907° C., in Fig. 5, $x = 0.8999$ for $P = 1.271$. P_0 in experiment 1 would then be 1.398 if the first horizontal in Fig. 7 is assumed to be an equilibrium state of the system Fe-Fe_3C, and gases. As there seems to be no other possible explanation, our first assumption should be correct. This is also the case with experiment 3, where 15.601 is obtained as the equilibrium constant of the carbon equilibrium. Then $x = 0.9362$ when $P = 1.136$ and $P_0 = 1.136 \times (2 - 0.9362) = 1.208$; by actual measurement P_0 was 1.207.

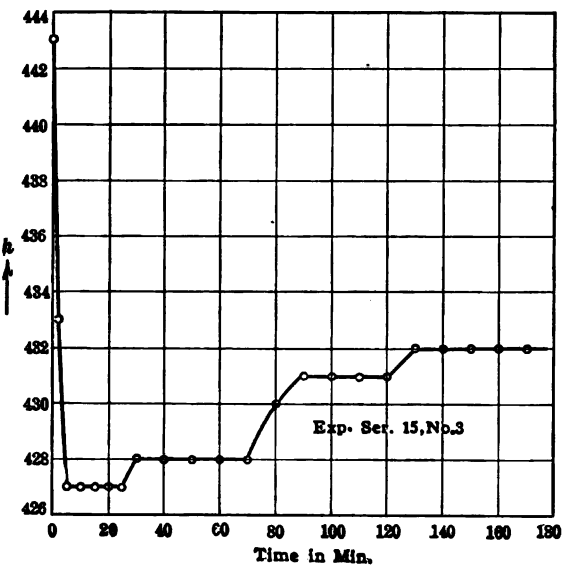


Fig. 8.—Experiment Series 15. Temperature 853° C.

The last (fourth) horizontals in Figs. 7 and 8 apparently correspond to the period during which reduction of iron oxide is effected without pressure change. Then the remaining horizontals (the second and the third) are presumably the equilibrium states of carburization; if that is assumed, a reasonable explanation may be made of the whole process of pressure change. The succession of reactions, considered in this way, may be expressed as follows:

Period of pressure decrease ..... $2CO \rightarrow C + CO_2$

Period of first pause ..... $\begin{cases} 2CO \rightleftharpoons C + CO_2 \\ FeO + CO \rightarrow Fe + CO_2 \end{cases}$

Period of first increase	$2CO \leftarrow C + CO_2$ $FeO + CO \rightarrow Fe + CO_2$ $3FeO + 5CO \rightarrow Fe_3C + 4CO_2$ $3Fe + 2CO \rightarrow Fe_3C + CO_2$
Period of second pause	$3Fe + 2CO \rightleftarrows Fe_3C + CO_2$ $FeO + CO \rightarrow Fe + CO_2$
Period of second increase	$3Fe + 2CO \leftarrow Fe_3C + CO_2$ $3FeO + 5CO \rightarrow Fe_3C + 4CO_2$ $FeO + CO \rightarrow Fe + CO_2$
Period of third pause	$3FeO + 5CO \rightleftarrows Fe_3C + 4CO_2$ $FeO + CO \rightarrow Fe + CO_2$
Period of third increase	$3FeO + 5CO \leftarrow Fe_3C + 4CO_2$ $FeO + CO \rightarrow Fe + CO_2$
Period of fourth pause	$FeO + CO \rightarrow Fe + CO_2$

In Figs. 9 and 10, the changes in gaseous state are roughly represented by arrowhead curves in the P-x diagrams, which are made out of the equilibrium constants obtained from the t-x diagram.

The last (final) equilibrium may be a trivariant in which a solid solution of FeO in Fe constitutes the solid phase, or it may be the divariant equilibrium corresponding to the FeO-Fe horizontal or even to the Fe_3O_4-

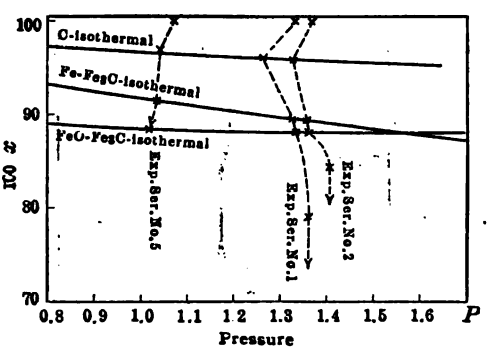


FIG. 9.—TEMPERATURE 907° C.

FeO horizontal, such as in Fig. 3, according to the conditions of the experiment. In all these cases, the final pressure should not be lower than the initial pressure. If the final equilibrium is the trivariant in which the solid phase is an oxygen-bearing iron containing some carbon, as in experiments 9 and 10 of series 8, the final pressure is lower than the initial.

The lowest pressure does not always occur in the carbon equilibrium; it may happen during any of the carburization equilibria. The following

results illustrate this statement. This result is represented in Fig. 11, to which the corresponding P-x diagram is attached.

EXPERIMENT SERIES 15—(*Continued*)

No. 4. Temperature, 772° C. Initial solid phase, 7.0848 gm. reduced iron containing 2.01 per cent. oxygen previously reduced and carburized with CO.

t	h	P	t	h	P	t	h	P
0	487	1.444	12	451		28	441	
1	470		13	451		29	441	
2	465		14	451		30	441	
3	460		15	448		35	441	
4	457		16	446		40	441	
5	455		17	445		50	441	
6	453		18	443.5	1.225	89	441	
7	451	1.257	19	443.5		90	444	1.223
8	451		20	443.5		100	444	
9	451		25	443.5		120	444	
10	451		26	443 5		150	444	
11	451		27	441	1.210			

In this case, the value of P_0 should be corrected from that corresponding to the supposed carbon equilibrium, as the fall of pressure at the beginning is so rapid that a delay of the initial time by a couple of seconds would cause an appreciable error in the result of measurement.

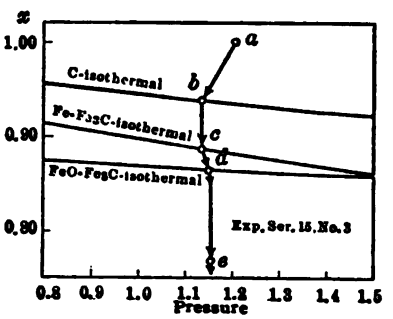


FIG. 10.—EXPERIMENT SERIES 15, No. 3. TEMPERATURE 853° C.

Since the coördinates of the point b in the P-x diagram are $x = 0.8295$ and $P = 1.257$,

$$1.257 \times (2 - 0.8295) = 1.471$$

is the corrected value of P_0 on an assumption that no oxidation had taken place during the soot deposition.

The second pause of pressure change occurs at a point the coördinates of which are $x = 0.8045$ and $P = 1.225$. This requires

$$P_0 = 1.225 \times (2 - 0.8045) = 1.465,$$

if the point c lies on the Fe-Fe_3C isothermal. This value of P_0 agrees accurately with the corrected value of initial pressure. As there are no other explanations to the phenomena, the assumptions should be correct. As a matter of fact, the curves ab and bc in Fig. 11 make a continuous curve, the equation of which is $xP = 1.471 - 2(1.471 - P)$. Then, the third pause in pressure change in this experiment must correspond to the period of FeO-Fe_3C equilibrium, and the pressure is lowest at this period, as shown in Fig. 11.

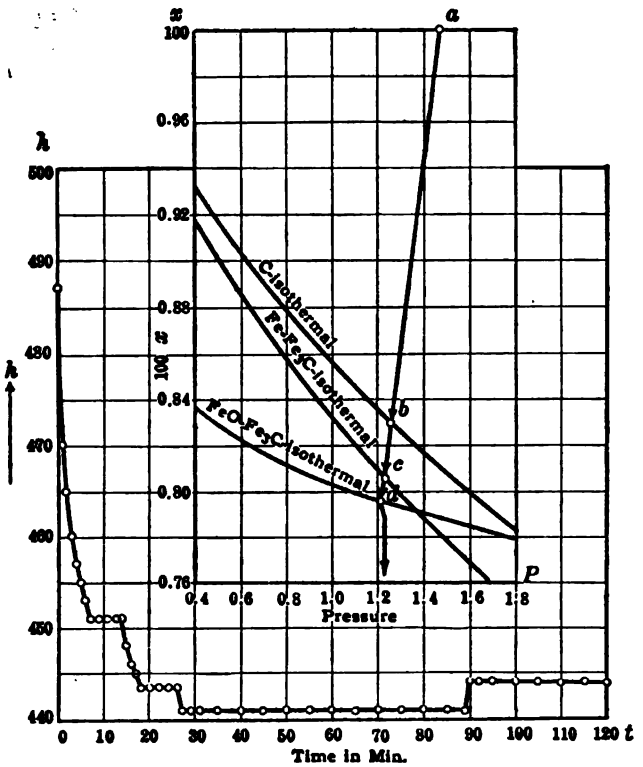


FIG. 11.—EXPERIMENT SERIES 15, No. 4. TEMPERATURE 772° C.

The actual magnitude of pressures in various states of equilibrium in this series of experiments may perhaps be complex functions of the composition of the solid phase, temperature, velocities of several reactions, etc. In general, the larger the oxygen content of the solid phase, the more pronounced is the displacement to the right of the equilibrium points in the P-x diagram, and the increase in pressure begins at the earlier period, hence the lowest pressure occurs at the earlier reaction of the series. A higher oxide of iron, especially when it is in a finely divided form, causes scarcely any depression of pressure at the instant when it is covered by CO in a confined space. If a solid phase contains such a small

quantity of oxygen that it causes a FeO-Fe_3C equilibrium when it is covered by CO, the third pause in the pressure change is the final state and the pressure always decreases from the first pause toward the last. When the solid phase is suitable to establish an Fe-Fe_3C equilibrium, the second pause is the final state, the pressure of which is always smaller than the first. An example is given below.

EXPERIMENT SERIES 15—(*Continued*)

No. 5. Temperature, 907° C. Initial solid phase, a well reduced and carburized iron oxide.

t	h	P	t	h	P	t	h
0	411	1.072	200	401.2		400	398
20	409.3		220	401.2		420	398
40	408		240	401.2		440	398
60	407		260	398	1.020	460	398
80	404.5		280	398		480	398
100	403	1.041	300	398		500	398
120	403		320	398		520	398
140	401.2	1.033	340	398		540	398
160	401.2		360	398		560	398
180	401.2		380	398		600	398

This result is expressed in the P-x diagram in Fig. 9. All these facts concerning the pressure change may be explained from the nature of the carburization equilibria, hence, vice versa, the former may be said to afford a proof to the latter.

Discussion of Result

The chemical equilibrium on the FeO-Fe_3C curve in the t-x diagram is one of the divariant system having three components and phases. Equilibrium is established when the oxygen-dissociation pressure of one of the two solid phases becomes equal to that of the gaseous phase, hence that solid phase must show a definite dissociation pressure at a definite temperature and pressure. For the sake of simplicity, this solid phase is denoted by S_1 and the other by S_2. But S_1 may be a solid solution of FeO in Fe and S_2 carburized iron, or S_1 may be an intermediate product of carburization containing Fe, C, and O, while S_2 is a solid solution of FeO in Fe with or without carbon content.

According to the first view, the ratio FeO:Fe in the solid solution is constant at a definite temperature and pressure, but increases with increase of pressure and temperature. When CO acts upon this, some part of it may be reduced and carburized, but the remaining part retains the

original ratio of FeO:Fe. For instance, if the ratio is expressed by $3:x$, the reaction may be represented by the equation

$$\underset{\text{solid solution}}{3FeO.xFe} + 5CO \rightleftharpoons \underset{\text{solid solution}}{xFe.Fe_3C} + 4CO_2$$
$$S_1 \qquad\qquad S_2$$

where x varies with temperature and pressure.

When nearly all of the S_1 is thus transformed to S_2 the remaining trace of S_1 may be dissolved by S_2. In that case the system increases its freedom by one and shows the transitional equilibria from the lower to the upper carburization curve. The only difficulty in this mode of interpretation is the assumption that $3FeO.xFe$ must react like a compound and that neither FeO nor Fe can react separately upon the surrounding gases.

According to the second view, S_1 is an intermediate product of carburization containing Fe, C, and O. It may be a solid solution of FeO with carburized iron, or Fe (or FeO) containing some quantity of the surrounding gas dissolved. If S_1 is such a substance, it can be easily imagined that its oxygen content, and consequently its oxygen pressure, varies concurrently with temperature and pressure. So long as S_1 exists in the system and its oxygen-dissociation pressure is larger than that of the surrounding gas, CO must first attack S_1; the latter must be reduced and CO_2 produced. This will, of course, alter the composition of S_1, and some amount of carburized iron must be separated. As no more than two solid phases can exist this carburized iron should go over the S_2 phase. S_2 is also attacked by CO as long as its oxygen pressure is larger than that of the gas phase. This will deprive S_2 of its oxygen (or FeO) content and supplies the S_1 phase with the new reaction product. The S_2 phase, in this way, loses its oxygen content step by step; hence its oxygen pressure is lowered in the same manner, but as long as it contains sufficient oxygen, some S_1 must be produced which keeps the composition of the gas phase constant if temperature and pressure are fixed.

The mechanics of reaction may be expressed as shown in Fig. 12. The mechanics of decarburization is exactly the reverse as shown in Fig. 13. The Fe-Fe_3C equilibrium is also one of the divariant system, but no solid phase showing oxygen pressure is on the left side of the equation

$$3Fe + 2CO = Fe_3C + CO_2$$

Therefore the existence of some solid phase showing a definite oxygen-dissociation pressure at a definite temperature and pressure must be assumed. Let this substance be designated R_1, and the other solid phase R_2. As to the composition of R_1 and R_2 and the parts played by them in the course of carburization, two possibilities may be considered. The

first is to assign R_1 to a solid solution of FeO in Fe, and R_2 to carburized iron. The ratio FeO:Fe in R_1 and, hence, the composition of gas

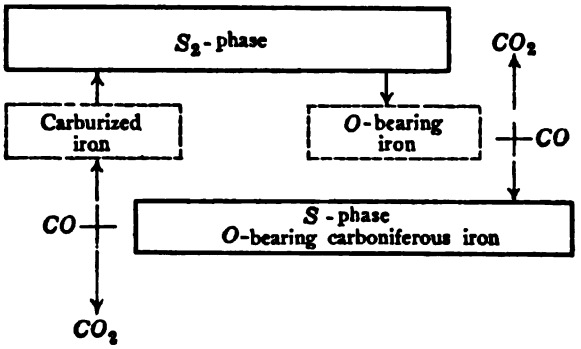


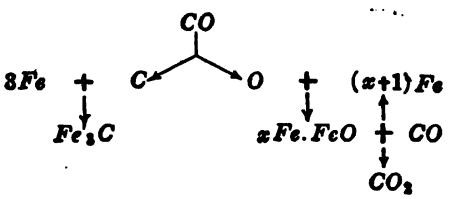
FIG. 12.—MECHANICS OF CARBURIZATION.

standing in equilibrium with it are to be considered constant if temperature and pressure are fixed. The mechanics of reaction are represented as follows:

$$x\text{Fe.FeO} + \text{CO} = (x+1)\text{Fe} + \text{CO}_2$$
$$\text{CO} = \text{C} + \text{O}$$
$$(x+1)\text{Fe} + \text{O} = x\text{Fe.FeO}$$
$$3\text{Fe} + \text{C} = \text{Fe}_3\text{C}$$

summing up $3\text{Fe} + 2\text{CO} = \text{Fe}_3\text{C} + \text{CO}_2$

Diagrammatically represented,



However, oxygen-bearing iron and carburized iron dissolve each other to a certain extent, as was proved by the existence of the trivariant carburization equilibria in experiment series 8. Then the existence of C in the R_1 phase considered in this way must be accepted.

According to the second view, R_1 contains carbon and is a solid solution of the type $x\text{Fe.}(u\text{Fe.}v\text{C.}w\text{O})$. This solid phase is attacked by CO as long as its oxygen-dissociation pressure is larger than that of the surrounding gas. But the reaction product should not constitute a separate phase—it must go over into R_2 phase. This at once shows that the new product is carbon-rich iron, which is dissolving into the phase of carburized iron (R_2). If one gram-atom of C is transferred to the R_2 phase as the result of the action of one molecule of CO, then R_1 phase requires one molecule of CO to compensate for the loss of one gram-atom of oxygen and one gram-atom of carbon in addition to the iron of which it

has been deprived; the latter should be supplied by the R_2 phase. In other words, one molecule of CO combines with the proper amount of iron

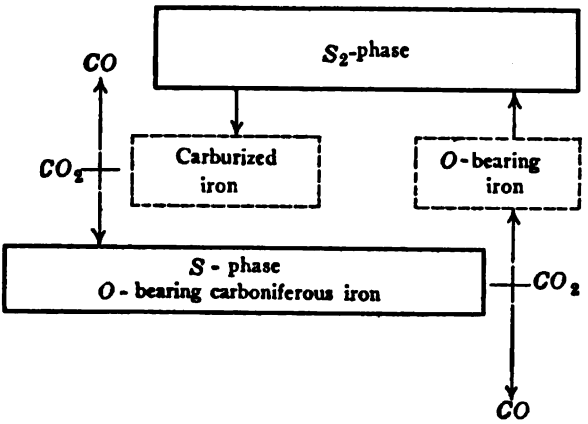


FIG. 13.—MECHANICS OF DECARBURIZATION.

of R_2 phase and joins with the remaining part of the R_1 phase to correct its dissociation pressure, which is constant in the system as long as the two solid phases exist therein. Then the result exactly coincides with the reaction

$$3Fe + 2CO = Fe_3C + CO_2$$

Then the part played by R_1 is entirely catalytic and the mechanism of the reaction may be expressed as follows:

$$(m\text{Fe}.v\text{C}.w\text{O}) + \text{CO} = [(m-a)\text{Fe}.(v-1)\text{C}.(w-1)\text{O}] + (a-3)\text{Fe}.\text{Fe}_3\text{C} + \text{CO}_2$$

$$a\text{Fe} + \text{CO} = \text{CO}.a\text{Fe}$$

$$[(m-a)\text{Fe}.(v-1)\text{C}.(w-1)\text{O}] + \text{CO}.a\text{Fe} = (m\text{Fe}.v\text{C}.w\text{O})$$

where

$$x\text{Fe}.(u\text{Fe}.v\text{C}.w\text{O}) \equiv [m\text{Fe}.v\text{C}.w\text{O}] \text{ and } m \geq a \geq 3$$

or as shown diagrammatically in Fig. 14. The reaction will continue until the supply of non-carburized iron from the R_2 phase is stopped when the remaining R_1 phase is destroyed by CO and is finally dissolved by R_2.

The existence of oxygen-bearing carboniferous iron is not altogether imaginary. H. M. Caron[7] proved the existence of oxygen in the carburized iron produced by the action of CO upon pure reduced iron. L. Gruner[8] obtained a similar result by employing iron wire instead of reduced iron. F. Giolitti and F. Carnevali[9], during the process of carburization of iron blocks, obtained thick crusts of oxygen-bearing

[7] *Compt. rend.* (1864) **59**, 335.
[8] *Compt. rend.* (1872) **74**, 226.
[9] *Jnl.* Iron and Steel Inst. (No. 2, 1911) 331.

iron covering the inner core of the carburized iron and intermingled with carbon. P. Georens[10] extracted gases from commercial steels by heating the latter in vacuum at high temperatures, and found the quantity of gas evolved to be three to four times the volume of steel when it was previously deoxidized and the chief constituent of the extracted gas to be carbon monoxide. This fact might well be explained by occlusion, but it may also be assigned to a decarburizing action of oxygen evolved by dissociation of a certain substance chemically combined with oxygen.

The present writer made the following experiment upon this point. About 20 gm. of pure iron oxalate was placed in a hard glass tube and well reduced by a slow current of hydrogen at a temperature slightly below 550° C., after which a slow current of CO was passed through, the tube being kept at the same temperature. At the first stage, the gas was vigorously absorbed by the iron so that none of the gas escaped from the end of the tube. After 1 hr. about one-fifth of the entering gas escaped from

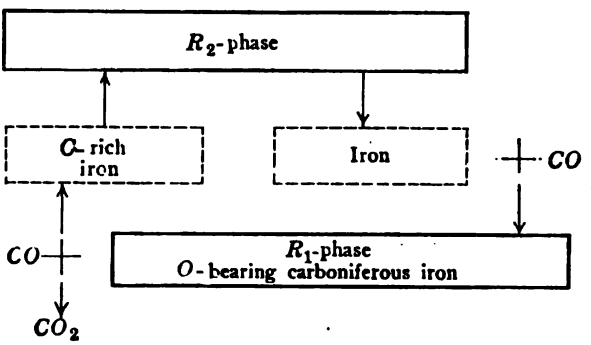


FIG. 14.—MECHANICS OF CARBURIZATION.

the tube. Though the absorption continued for several hours it gradually decreased. The escaping gas was introduced into a hard glass tube which was heated by a gas flame to below dull redness; this caused a black substance to be deposited at the hot part of the second tube. This black substance was strongly attracted by a magnet and some of it dissolved in aqua regia with evolution of gas leaving carbon flakes. The solution then showed iron content.

The black deposit was apparently a decomposition product of some volatile substance resembling iron carbonyls in character. At the hot part of the first tube, the decomposition should have been strong and several complicated reactions between gas and solid may be supposed to have taken place; only a small part of reaction products might have escaped into the second tube.

All of these facts, especially the phenomenon of gas absorption together with the indication of gas reaction upon reduced iron in the above

[10] *Mitteilungen aus den Eisenhüttenmannischen.* Institut der Königl. Tech. Hochschule, Aachen, 1910.

experiment, induced the author to believe that the formation of the oxygen-bearing carboniferous iron, such as R_1 or S_1, is possible, for the reaction under the above conditions of experiment is, in some respect, the same as that which takes place at the higher temperature and under very high pressure as is easily understood from Fig. 6.

Limit of Carburization Temperature and Pressure

The disposition of the FeO-Fe_3C curve in Fig. 5 shows that the latter will approach very closely to a horizontal $x = 1$ at a temperature of about 1300° C. This shows the following facts:

1. At a temperature of about 1300° C., the oxygen dissociation pressure is equal to that of pure CO if the pressure is one atmosphere.

2. At a temperature higher than about 1300° C., the carburizing action of CO does not occur; carburized iron is oxidized to FeO-Fe solid solution even by a current of pure CO under a pressure of one atmosphere.

3. The above limit of temperature increases slightly with increase of pressure.

The Fe-Fe_3C curve in Fig. 5 seems to approach very closely to a horizontal $x = 1$ at a temperature of about 1200° C. Then

1. At a temperature of about 1200° C. the dissociation pressure of R_1 is equal to that of CO, and neither carburization nor decarburization occurs even in a current of pure CO if the pressure is one atmosphere.

2. At a temperature between 1200° and 1300°, and under a pressure of one atmosphere, the dissociation pressure of pure CO is larger than that of R_1 but is smaller than that of S_1; carbon-bearing iron is decarburized even by a current of pure CO, but oxygen-bearing iron may be carburized by the same gas; both reactions end in the formation of oxygen-bearing carboniferous iron proper to that temperature.

3. At a temperature between 1200° and about 695° C., a gas richer in CO than corresponds to the Fe-Fe_3C curve in Fig. 5 will carburize iron under a pressure of one atmosphere or more. Under the lower pressures, both the lower and higher boundaries of temperature are correspondingly decreased, but under the higher pressures the reverse holds true.

4. The lower the pressure, the larger is the value of x at equilibrium, hence purer gas (richer in CO) is required for carburization; the higher the pressure the easier is the carburization; *i.e.*, the same degree of carburization may be accomplished by less pure gas, compared with the case of lower pressure—if the same gas is employed, the velocity of reaction is greater in the case of higher pressure.

5. Under a pressure higher than that corresponding to the curve *E-F* in the *P-x* diagram (Fig. 6), the first carburizing reaction taking place after the reduction of oxide with CO is

$$3Fe + 2CO = Fe_3C + CO_2.$$

Under a pressure higher than that corresponding to the curve *G-H* in the same diagram, the carburizing reaction according to the above equation occurs upon iron oxide the oxygen pressure of which is higher than that corresponding to a saturated solution of Fe in FeO.

6 At a temperature below 695° C and under a pressure of one atmosphere or more, the carbon isothermal sinks beneath the two carburization isothermals in the *P-x* plane, and no carburization, in the ordinary sense, can occur.

7. All the conditions of decarburization are just the reverse of those of carburization.

Applications of Theory of Carburization

Casehardening

That part of the casehardening theory of Giolitti and Carnevali[11] that is related to the present research may be summarized as follows:

1. As iron carbide dissolves in iron above 700° C., the mixed crystal may show several carburization curves, according to the content of carbon in iron as represented by *a*, in Fig. 15.

2. One of these curves may coincide with the carbon isothermal throughout its entire length; the mixed crystal of that composition is designated as the "Σ-mixed crystal."

3. If the gaseous condition in the reaction vessel always corresponds to a point on the carbon isothermal, the carburizing action of the gas converts the whole iron into the Σ-mixed crystal.

4. Under a pressure higher than the point *O*, Fig. 15, the formation of magnetic oxide must accompany that of the Σ-mixed crystal; within the range of pressure between *O* and *Q*, the formation of ferrous oxide must accompany that of the Σ-mixed crystal; under a pressure lower than *Q*, the Σ-mixed crystal alone is formed, hence the carburization must be performed under a pressure lower than *Q*.

5. Curves *3*, *4*, and *5* displace toward the right concurrently with rising temperature as the result of which *O* and *Q* displace toward the right and higher pressure: therefore carburization may be performed at higher pressures without oxidation. The displacement of *O* and *Q* is controlled by the composition of the iron.

It is at once evident that there can be no such *P-x* diagram as that shown in Fig. 15. The meeting of curves *1*, *2*, and *3* at one point occurs only at 695° C. and curve *5* also passes through the same point. The carbon isothermal lies to the left of one or both of the carburization curves under a pressure of one atmosphere or more at temperatures lower than 695° C.; in this case no carburization is possible. This error is due to the basing of these curves upon the theory of Schenck that curves *1*, *2*,

[11] *Jnl.* Iron and Inst. Steel (No. 2, 1911) 307–352.

and S must always pass through a common point. Therefore, Giolitti and Carnevali's Σ-mixed crystal, which, at the temperatures suitable for carburization, should be nothing other than iron saturated with carbon, was always obliged to show a higher oxygen pressure than that corresponding to the Fe-Fe_3C isothermal. The oxygen pressure should be reduced to that of the carbon isothermal when the carburization is finished.

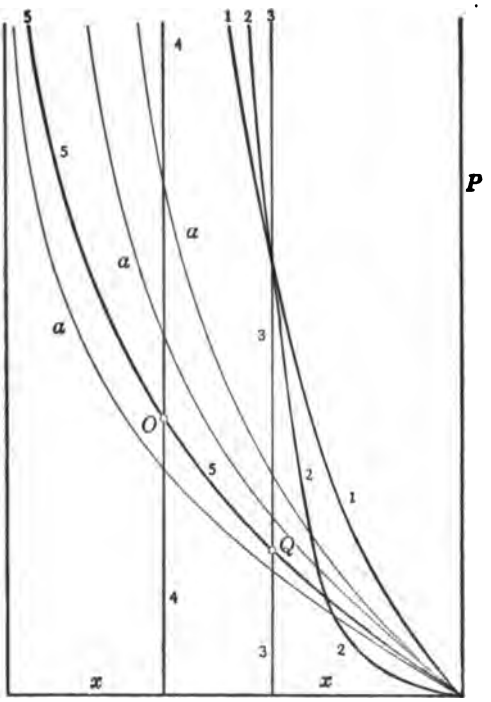


FIG. 15.—FROM GIOLITTI AND CARNAVALI.

1. Fe-Fe_3C isothermal.
2. FeO-Fe_3C isothermal.
3. FeO-Fe isothermal.
4. Fe_3O_4-FeO isothermal.
5. C isothermal.

The present author offers as a typical P-x diagram for carburization temperatures Fig. 16, which is a P-x diagram for 950° C.; the upper three isothermals were plotted from the corresponding equilibrium constants. Carburization of iron is possible at 950° C., for instance, in a CO and CO_2 mixture containing more than about 75 per cent. CO and less than six atmospheres total gaseous pressure; under a pressure of twelve atmospheres, the necessary amount of CO decreases to about 63 per cent. If the mixed gas is richer in CO than that corresponding to any point on the carbon isothermal, there is soot deposition together with carburization.

In other words, a point on the carbon isothermal represents those values of P and x at which soot can exist in the system.

It is highly probable that some substance showing the same oxygen pressure as that of the gaseous phase is formed in the solid phase if an equilibrium is established at any one point on the carbon isothermal. But if the gaseous phase is always richer in CO than that corresponding to that point equilibrium is never established there, hence any fixation of oxygen in the solid phase is avoided even under the pressure represented by the same point. For instance, the point Q never represents the pressure under which FeO should be formed in carburized iron under every circumstance of the gaseous phase. Then why has Giolitti and Carnevali's experiment proved the formation of a thick stratum of compact crust of magnetite on the carburized iron?

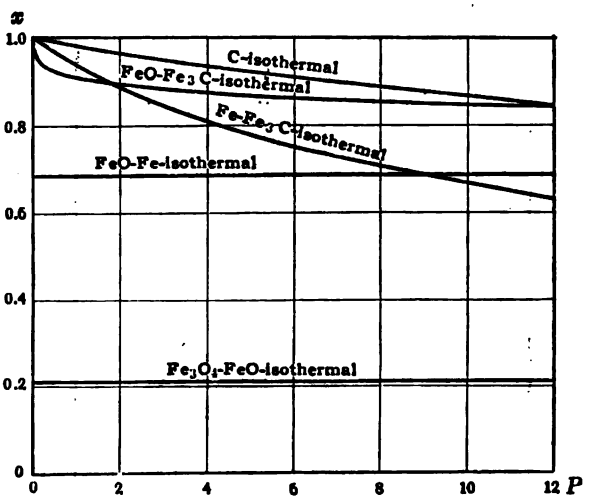


FIG. 16.—P-x DIAGRAM FOR 950° C.

In order to solve this problem, let us make a few calculations. As their experiments were made between 890° and 960° C., assume that it was fixed at 900°. Then, calculating from the value of K_1, it is known that R_1 must show a dissociation pressure corresponding to $x = 0.47$ under the pressure of 25 atmospheres. Even if it is assumed that R_1 is pure iron oxide, its oxygen content does not exceed 23.5 per cent. at 1075° C., and 23.9 per cent. at 863° C. (see Figs. 3 and 4); by graphic interpolation, it is found to be about 23.8 per cent. for 900° C., hence the iron content of the oxide, which is a solid solution of Fe_3O_4 in FeO, must be at least 76.2 per cent. If any higher oxide is present in the system, no carburization should be possible.

An analysis of the crust made by the same authors, however, showed 69.2 per cent. Fe, so that the crust presumably contained some combined

carbon and the oxygen pressure of the former must have been decreased by the latter, otherwise the gas must have acted as a decarburizer instead of a carburizer.

If it was magnetic oxide, or very nearly magnetic as reported by the authors, this might be due to their method of carburization. Giolitti and Carnevali's method of casehardening is accomplished by the action of a so-called mixed agent on heated iron. The mixed agent consists of charcoal, which surrounds the iron block, and a current of CO_2 passed through the reaction vessel with a definite velocity. This mixed agent may produce CO quickly, but the gaseous currents, rich in CO_2, have every chance to touch the heated iron before they are converted to CO causing serious oxidation of the iron. Of course the carburization may go on as long as the gas that touches the surface of the iron is richer in CO than corresponds to the Fe-Fe_3C isothermal, but a gas with a large CO_2 content not only facilitates the formation of R_1, but also decreases the carburization velocity in a marked degree because the difference between the percentage of CO in the gaseous current and that of the gaseous phase in its equilibrium state in a closed vessel should be a factor in determining the velocity of the reaction. As a matter of fact, the reducing action of carbon upon CO_2 is not completed as instantaneously as was expected by the authors, especially at a temperature of 900° or 800° C.

The best practical method is the rapid introduction of CO, instead of CO_2, upon the heated iron with or without carbon enclosure (according to the result required) under as high a pressure as possible. The remaining problem is then the industrial preparation of pure CO. Fortunately the percentage of CO_2 in the escaping gas from the reaction vessel is very small, especially when the velocity of the passing gas is large; hence if the CO_2 content of the escaping gas is reduced by passing this gas through a furnace filled with highly heated carbon, CO_2 may be completely reduced in a short time. The resulting CO is then returned into the reaction vessel. In order to accomplish this operation quickly and completely, the furnace must be kept at high temperature. But the temperature of the carburization vessel should not be kept very high for the carburized iron should not be brought to melting. Moreover, even in the temperature range of 1100° to 1200° C., carburization by the gas reaction is difficult unless we work under fairly high pressures. From the practical standpoint, too, the heating of the carburization vessel to a high temperature like 1100° is not easy to carry out.

On the other hand, the pressure in the furnace for the purification of gas should be low, otherwise the prepared gas would be impure, as is easily understood from the disposition of the carbon isothermals, while the pressure in the carburization vessel should be high enough to facilitate the quick carburization. Therefore the claims of these two reactions are,

to some extent, contradictory to each other; they should not be carried out in the same vessel.

Malleable Casting

That which it is desired to oxidize in the practice of malleablization is iron carbide and not iron itself. The reaction should, therefore, be confined to

$$Fe_3C + CO_2 = 3Fe + 2CO$$

and not to be extended to

$$Fe + O = FeO, \text{ etc.}$$

Then, it is clear that the oxygen-dissociation pressure of the gas surrounding the cast iron that is to be malleablized should be always a little higher than corresponds to the Fe–Fe_3C curve in the t-x diagram proper to the adopted pressure; any large excess of oxygen pressure should be avoided, as otherwise iron would be oxidized. This regulation of pressure can be performed by one of the following methods:

1. By the regulation of the velocity at which CO_2, O_2, or air is introduced into the reaction vessel.

2. By the regulation of the composition of the oxidizing gas; for instance, the ratio of $CO:CO_2$ when a mixture of these gases is employed, the ratio of $O_2:N_2$ when air is employed, etc.

3. By the combination of these methods.

By the analysis of the escaping gas the oxygen pressure of the reacting gas is easily determined, it is only necessary to determine the ratio $CO:(CO + CO_2)$ in the gas, for the volume percentage of oxygen is negligible.

Reactions Between Iron, Oxygen, and Carbon in an Iron Blast Furnace

This discussion will be confined chiefly to gas reactions taking place between Fe, O, and C, and will take into consideration neither the influences of the other substances nor the reactions arising between them. Moreover, the study is, in a sense, of a special nature, being confined to an individual furnace, for the conditions may vary in different furnaces; even in the same furnace, they may differ in accordance with the nature of the charges and the mode of operation. Hence only an example, to show the method of investigation, will be given. In this case three kinds of data relating to the conditions of the blast furnace come into consideration: (1) Distribution of pressure, (2) distribution of temperature, and (3) gaseous composition with regard to the height in the furnace. The first was neglected by several previous investigators owing chiefly to the difficulty of measurement; therefore a few approximate assumptions must be made. The iron blast furnace of Gutehoffnungshütte in Oberhausen, whose blast-furnace diagram was determined by W. A. Schlesinger,[12]

[12] *Stahl u. Eisen* (1911), 1182.

is adopted. It is regretted that the author did not report the percentage of CO and CO_2 in the total gas taken in analysis. In some furnaces this percentage decreases from the lower part toward the top while in others the reverse is the case. Commonly it varies between 34 and 38 per cent.—a variation that has little significance in the calculation of partial pressure of these two gases as compared with the error arising from the calculation of the total pressure. Therefore, it will be assumed to be 36 per cent. and that no variation in this percentage took place throughout the height of the furnace.

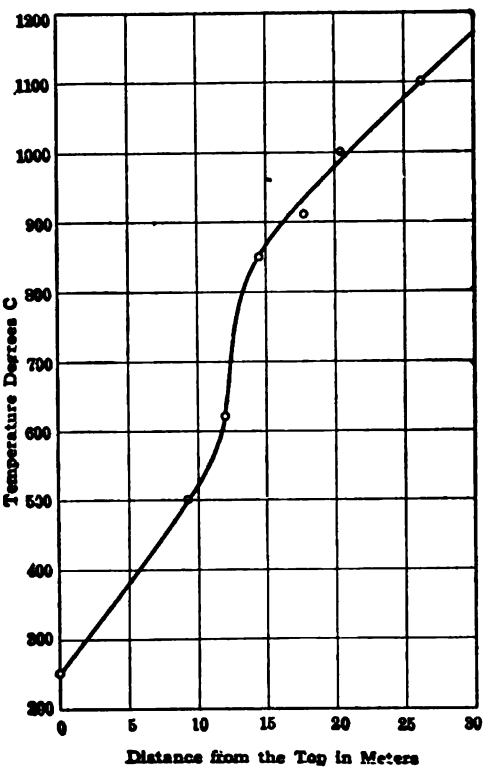


FIG. 17.—DISTANCE-TEMPERATURE CURVE.

The pressure of the blast was reported to have been about 60 cm. (Hg), which corresponds to 1.776 atmosphere in net value; the wind pressure at the top of an ordinary blast furnace having this blast pressure may properly be assumed to be about 200 mm. in water column;[13] this corresponds to a net value of 1.019 atmosphere. The decrease of pressure is, therefore, 0.757 atmosphere. Assume that the pressure at the tuyere level is 1.776 atmosphere and that the decrease of pressure is

[13] Osann: *Eisenhüttenkunde* (1915) **1**, 380.

proportional to the height of the furnace as a first approximation although it may perhaps be a complex function of temperature, distance from the tuyere level, inner diameter of the furnace, velocities of the chemical reactions, etc. The accompanying table specifies the pressure distribution in this furnace at the time that Schlesinger made his measurement.

Distance from Top, Meters	Temperature, Degrees C.	Total Pressure, Atmospheres	Partial Pressure of CO-CO_2 Atmosphere
27.8		1.776	
26.2	1100	1.732	0.624
20.4	1000	1.574	0.567
18.5	950	1.523	0.548
16.4*	900	1.466	0.522
14.5	850	1.414	0.509
13.5*	800	1.387	0.499
12.8*	750	1.367	0.492
12.4*	700	1.357	0.489
12.1*	650	1.348	0.485
12.0	620	1.346	0.485
11.7*	600	1.338	0.482
9.2	550	1.269	0.457

* These numbers were found from the distance-temperature curve shown in Fig. 17.

The equilibrium gaseous compositions of several reactions occurring at the various heights of the furnace may be found by interpolation from Figs. 5, 6, and 13.

Distance from Top, Meters	Temperature, Degrees C.	Equilibrium Composition of Gas, Per Cent. CO in CO-CO_2 in				
		Fe_3O_4-FeO Equilibrium	FeO-Fe Equilibrium	FeO-Fe_3C Equilibrium	Fe-Fe_3C Equilibrium	C Equilibrium
26.2	1100	15.8	73.0	95.6	98.9	
20.4	1000	19.8	70.0	92.9	97.0	99.6
16.4	900	23.5	67.0	90.3	95.4	98.3
14.5	850	26.2	65.4	88.6	94.5	97.0
13.5	800	29.6	63.8	86.0	92.3	94.4
12.8	750	33.2	62.2	79.0	87.0	88.3
12.4	700	36.7	60.2			73.8
12.1	650	40.4	60.0			50.3
11.7	600		55.6			30.3
9.2	550		52.9			

Each of the equilibrium curves may be plotted from this table on the blast-furnace diagram drawn by Schlesinger as shown in Fig. 18:

Curve I is an equilibrium curve of reaction $Fe_3O_4 + CO \rightleftharpoons 3FeO + CO$
Curve II is an equilibrium curve of $FeO + CO \rightleftharpoons Fe + CO_2$
Curve III is an equilibrium curve of $3FeO + 5CO \rightleftharpoons Fe_3C + 4CO_2$
Curve IV is an equilibrium curve of $3Fe + 2CO \rightleftharpoons Fe_3C + CO_2$
Curve V is an equilibrium curve of $2CO \rightleftharpoons C + CO_2$.
Curve VI represents the actual gaseous composition measured by Schlesinger.

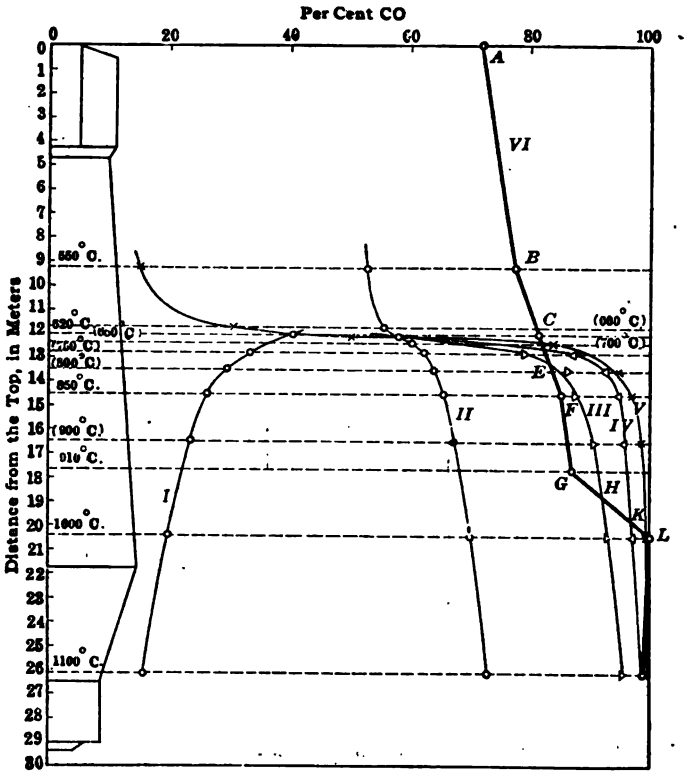


FIG. 18.

That part of curve VI corresponding to temperatures lower than 910° C. is quite similar to the FeO-Fe curve, showing that the main part of the reducing power of this blast furnace is used for the reduction of ferrous oxide. Ferrous oxide is difficult to reduce owing to its low dissociation pressure, while the reductions of ferric oxide and magnetic oxide are easier because of their high dissociation; the removal of oxygen, corresponding to about 24 per cent. of the original oxygen content will convert the latter wholly into a mixture of ferrous oxide and iron.

The form of the curve IV, however, must be affected by the following factors: (1) Evolution of CO_2 from limestone; (2) reaction of soot de-

position; (3) reduction of higher oxides; (4) carburization; (5) reducing action of C upon CO_2.

For the dissociation pressure of $CaCO_3$, J. Johnstone[14] gave the following numbers:

Temperature, Degrees C.	Pressure, Mm. Hg.	Temperature, Degrees C.	Pressure, Mm. Hg.
1000	2710	750	68.0
950	1490	700	25.3
900	773	650	8.2
850	373	600	2.35
800	168		

Comparing these values with the partial pressure of CO_2 and the total pressure of the gaeous flow in the blast furnace, gives the values shown in the accompanying table where the partial pressures of CO_2 were calculated from curve VI.

Distance from Top, Meters	Temperature, Degrees C.	Partial Pressure of CO_2, Mm. Hg.	Total Pressure, Mm. Hg.	Dissociation Pressure of $CaCO_3$ Mm. Hg.
26.2	1100	10	1316	
20.4	1000	0	1192	2710
18.5	950	38	1158	1490
16.4	900	56	1114	773
14.5	850	58	1075	373
13.5	800	63	1054	168
12.8	750	66	1039	68
12.4	700	67	1031	25
12.1	650	70	1025	8
11.7	600	70	1017	2
9.2	550	78	964	

By graphic interpolation, it is known that the decomposition of limestone begins at about 12.8 m. from the top and that the strong decomposition begins at about 17.3 m. (very near to zone *G*). Since there is no partial pressure of CO_2 at zone *L*, Fig. 18, the decomposition should be finished at least before the charge reaches that zone. Hence the interval between these two zones *G* and *L* should be a zone of strong decomposition of limestone. The sudden fall of curve VI at this zone causes the belief that there may be some connection between these two facts. A number of other blast-furnace diagrams show this kind of break in the curve, and the type of curve shown in Fig. 18 seems to represent the most common and normal state of an iron blast furnace. A diagram of a blast furnace in Oberschlesich made by Nietz (Doktor Dissertation, Aachen) and the diagrams quoted by C. Brisker[15] show this kind of break in the curves

[14] *Jnl.* Amer. Chem. Soc. (1910) **32**, 944

[15] *Stahl u. Eisen* (1908) **1**, 391.

although the degree and position of the break may differ in different furnaces according to the velocity of wind, distribution of temperature and pressure, nature of charge, etc.

Another possible explanation of that portion of curve VI is that it corresponds to the uppermost steep portion in the equilibrium curves in Figs. 2, 3, and 4; in other words, ferrous oxide ceases to be a definite solid phase at the point *G* and the subsequent reduction is that of the solid solution of ferrous oxide in iron, which should cause a gradual rise of the curve VI. This transition, however, takes place gradually, as in Fig. 4, etc., so that it may not cause such a sudden change of the gaseous composition though it may have some influence upon it. Therefore this break of the curve is presumably an indication of the sudden deterioration in the quality of gas resulting from sudden decomposition of limestone.

The reaction of soot deposition takes place about 12 m. from the top of the furnace. "Das Hängen," if any, must occur in or above this zone. This reaction may have some influence on curve VI, as C. Brisker has generalized from the instances of several other furnaces, but it must be remembered that the deposited soot is oxidized immediately after the charge has traversed the zone about 12.5 m. from the top so that the effect of this reaction on the gas flow may compensate that of the soot deposition. That part of the latter which lies above point *G* seems to be determined chiefly by the disposition of the Fe-FeO curve.

The reduction of higher oxides may occur even in that part of the zone in which the soot deposition begins. But the reaction cannot be conspicuous and its effect on the form of curve VI is naturally very small because curves I and II are high and the velocities of reactions are small on account of low temperatures. The strong reduction of the higher oxides begins as soon as the charge has passed through the zone at which the oxidation of soot begins. The reaction may be finished in a short distance on account of its enormous velocity; the nature of the reaction resembles that of the decomposition of limestone. Perhaps the steep inclination of the curve between points *B* and *F* has an intimate relation with this reaction.

The reactions of carburization may take place 12.5 to 13 m. from the top (*C* to *E*). Any carbon fixed in this zone is thoroughly oxidized afterward and no carburization occurs until the charge arrives at zone *H*, which is about 18.7 m. from the top. Here the carburization of FeO may begin while at zone *K*, which is about 19.75 m. from the top, the carburization of iron may take place. At the tuyere level, the temperature is too high for the existence of iron carbide, so the carbon content in iron may be oxidized by the blast. But the reaction between carburized liquid iron and the surrounding gas is entirely beyond the scope of the present research.

As the result of the rapid carburization at the lower part of the furnace, a large quantity of CO_2 may be produced; this may have some influence upon the sudden depression of that part of curve VI between *G* and *L*.

At the lower part of the furnace, coke is able to convert oxygen or CO_2 into CO very rapidly on account of the high temperature. According to van Voltens[16] the free oxygen, which is so strongly blown in, can exist as

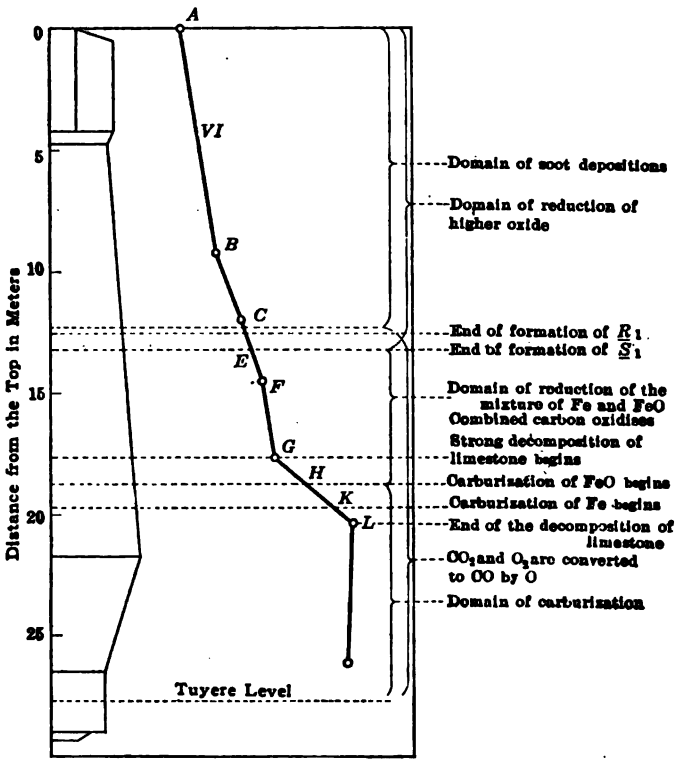


FIG. 19.

such only in a space 60 cm. in diameter around the tip of the tuyere; the region in which CO_2 can exist seems to be a little larger. At any rate, the combustion of free carbon, together with the velocity of the blast, must be the most potent factors determining the position of curve VI, while the reduction of ferrous oxide and the decomposition of limestone are other prominent factors which determine the disposition of the same curve.

The foregoing may be summarized in the diagram shown in Fig. 19. It must be remembered that all the boundaries of reactions must devi-

[16] *Stahl u. Eisen* (1893) 26.

ate in some degree from those represented in this diagram according to the velocity of the blast. In other words, curve VI, which illustrates the reactions, should lag upwards.

Problem of Quick Smelting

It is well known that increasing the blast pressure accelerates smelting. In some modern American iron blast furnaces, especially those built during the war, such pressures as 1200 gm. per sq. cm. are said to have been adopted in order to increase the capacity of the furnace. There may be many reasons why smelting is accelerated by increasing blast pressure, but here it will be considered only from the standpoint of the gas reactions.

By increasing the blast pressure, the following changes in the gas flow may be expected to occur: The velocity of gas flow in the furnace is increased; the partial pressure of the reacting gas is increased; and the range of high temperature in the furnace is extended toward the top.

It is scarcely worth while to consider that the range in which the free oxygen or CO_2 exists around the tip of the tuyere is extended by increasing the blast pressure, for, should this happen, it would be a negligible enlargement of the space especially when the temperature of the glowing carbon is increased by that operation.

The increased velocity of gas flow displaces the actual gas-composition curve in the blast-furnace diagram upward and leftwards; consequently it enlarges the distances from that curve to every other equilibrium curve, and these enlargements should increase the reaction velocities. Moreover, the increased velocity of gas flow extends the zone in which final carburization may be effected, which necessarily results in quicker smelting.

The extension of the high-temperature zone increases that part of furnace where the reduction and the carburization can be made effectively, thus shortening the "pass-through time."

The increase of the partial pressure of $(CO + CO_2)$ is also desirable for it lowers the position of the carburization curves and hence causes the increase of carburization velocity. Even the simple reduction of oxides should be accelerated by this change on acount of the increase of concentration of CO in $(CO + CO_2)$.

Perhaps the quick smelting in some modern furnaces is attributable chiefly to the combined effect of the conditions enumerated. However, the introduction of nitrogen in the furnace is not advisable, if considered from a purely scientific standpoint. Oxygen or the exhaust gas mixed with a suitable quantity of oxygen instead of air, would be effective, because, in this way, it is possible to maintain the partial pressure of $(CO + CO_2)$ nearly 100 per cent. of the total pressure, which will lower the posi-

tion of carburization curves in the blast-furnace diagram in a marked degree. Moreover, the ratio of CO_2 produced by the reactions to that of CO would always be very small, hence the actual gas composition curve would be raised much higher than the ordinary position. In an electric iron smelting furnace the realization of this condition is relatively easy.

Summary

1. Equilibrium compositions of gas phase in the system CO, CO_2, and Fe containing more than a few per cent. of oxygen were measured at 863 C., 1070 C., and 1175 C.

2. Equilibrium compositions of gas phase in the system (*a*) CO, CO_2 FeO (saturated with Fe), and Fe (saturated with FeO) and (*b*) CO, CO_2, Fe_3O_4 (saturated with FeO), and FeO (saturated with Fe_3O_4) were measured at several temperatures higher than 700 C.

3. Pressures in the above two equilibrium systems containing free carbon as a permanent solid phase were calculated.

4. Dissociation pressures of FeO (saturated with Fe) and Fe_3O_4 (saturated with FeO) were calculated.

5. Equilibrium composition of gas phase in the systems (*a*) FeO, Fe_3C, CO, and CO_2 and (*b*) Fe, Fe_3C, CO, and CO_2 were measured in a temperature range of 700° to 1100° C. The formation of oxygen-bearing carboniferous irons and the mechanism of carburization were inferred.

6. The compositions of gas phase in the carburization equlibria under various temperatures and pressures were calculated.

7. Some applications of the carburization theory on the practice of casehardening, malleable casting, and the explanation of blast-furnace diagram etc. were treated.

Acknowledgments

The author is under great obligation to Prof. M. Chikashige, of the Imperial University of Kioto, for the care and attention he has bestowed on the research work.

The cordial thanks of the author are also due to Dr. R. B. Sosman of the Geophysical Laboratory, Washington, D. C., and Professor K. Ikeda, of the Tokyo Imperial University, for their valuable advice and interest.

DISCUSSION

Haakon Styri,* Philadelphia, Pa.—It is interesting to see that Mr. Matsubara's data on the dissociation pressures of FeO confirm calculations made by Professor LeChatelier about ten years ago. I have

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* Chief SKF Research Laboratory.

used LeChatelier's data to calculate the equilibrium conditions in the steel furnace for various concentrations of oxygen, carbon, manganese, and silicon. We are greatly in need of more accurate data about these equilibrium conditions and it would be extremely valuable if Mr. Matsubara, or somebody else, could undertake to establish equilibrium at higher temperatures than were here experimented with, including temperatures higher than the melting point of iron.

J. W. RICHARDS,* South Bethlehem, Pa.—Mr. Styri says that we should know the equilibria at higher temperatures. If the equilibria pressures at lower temperatures are known, it is possible, in general, to make a pretty good estimate of the pressures at the higher temperatures. The dissociation pressures of iron oxides will follow the same type of formula; *viz.*, $\log p = -\frac{A}{T} + B$. If the logarithm of the pressure is plotted against the reciprocal of the absolute temperature, the dissociation pressures will lie on a straight line, and can be readily extrapolated from low temperatures to higher ones.

G. K. BURGESS,† Washington, D. C.—That applies, I understand, where you have one phase. These temperatures were for substances in a solid state. If you go from the solid to the liquid phase, would you not get the same sort of a curve we had before, and might that not lead you into error?

J. W. RICHARDS.—Certainly; one formula is only valid for substances in the same physical state. If the physical states change, another formula of the same form but with different constants appears.

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* Professor of Metallurgy, Lehigh University.

† Chief, Division of Metallurgy, Bureau of Standards.

Physical Changes in Iron and Steel below the Thermal Critical Range

By Zay Jeffries,* D. Sc., Cleveland, Ohio

(New York Meeting, February, 1920)

It has been known for centuries that iron and steel could be hardened by cold hammering and that the metal could be restored to the normal condition by heating to a red heat and cooling, either rapidly or slowly with nearly pure iron, but slowly with steels containing considerable carbon. The art of tempering steels is also very old. When a medium- or high-carbon steel is quenched from a cherry-red heat, the hardness is increased; this hardness can be reduced by heating to various temperatures below the lower thermal critical point, which is near 700° C. The present paper will not consider these old and well known changes in iron and steel below the thermal critical range but will confine itself to the more unusual changes, some of which have been studied recently. Stromeyer,[1] for example, in 1886, reports that both working steel and heat treatment of steel in the blue-heat range are highly injurious. Recently, however, some metallurgists believe that the straightening of warped steel forgings at a blue heat produces a beneficial effect on the metal.[2]

The Engineering Division of the National Research Council has constituted a committee on Physical Changes in Iron and Steel below the Thermal Critical Range, which has the following personnel: R. R. Abbott, H. C. Boynton, William Campbell, J. V. Emmons, F. B. Foley, H. J. French, H. M. Howe, Zay Jeffries (chairman), F. C. Langenberg, J. A. Mathews, P. D. Merica, A. H. Miller, J. H. Nelson, G. A. Reinhardt, W. E. Ruder, H. F. Wood. This committee is studying several aspects of the physical changes in iron and steel. The results, reported in the literature and obtained by recent experimentation, will be given; this will be followed by a general theoretical discussion of the more important

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[1] C. E. Stromeyer: Injurious Effect of a Blue Heat on Steel and Iron. *Proc.* Inst. Civil Engr. (1885–86) **84**, 114.

[2] F. C. Langenberg: Private communication.

observations outlined. Finally, the commercial importance of this subject will be briefly considered.

General Observations

Tensile Properties of Iron and Steel below the Thermal Critical Range

The tensile strength of nearly pure iron, such as Armco iron or wrought iron, is about 40,000 to 50,000 lb. per sq. in. (2812 to 3515 kg. sq. cm.) at room temperature. The strength increases with rising temperature up to about 200° to 250° C.; the maximum strength is usually 15 to 25 per cent., and in one instance 37.6 per cent.,[3] greater than that at room temperature. The strength increases gradually, from a minimum, throughout a temperature range of about 200° C. and then decreases gradually for an additional 100° C.; after this, the rate of decrease of strength with increase in temperature becomes rapid. These results are reported by Martens,[4] Speller,[5] Epps and Jones,[3] Lea and Crowther,[6] Bach,[7] and Howard.[8] The tensile properties of Armco iron, with the exception of the elastic limit, are given in another communication by the present author.[9] In Howard's work, the tensile properties of steels with varying carbon content are given. He gives the tensile strengths of steels containing 0.09; 0.20; 0.37; 0.57; and 0.97 per cent. carbon, all of which show gradual increase up to 250° to 300° C. It seems that the greater the carbon content, the greater is the magnitude of the increase; but the high-carbon steels do not necessarily show as large an increase in percentage of strength as the low-carbon steels.

The elastic limit of iron and steel at elevated temperatures is reported, by Martens, to be the same at 250° C. as at room temperature, passing through a maximum at about 200° C. Howard, on the other hand, states that the elastic limit of steel decreases continuously with a rise in temperature. Huntington[10] gives elastic-limit determinations at elevated

[3] F. A. Epps and E. O. Jones: Influence of High Temperature upon Elastic and Tensile Properties of Wrought Iron. *Met. & Chem. Eng.* (1917) **17**, 67.

[4] Martens: Influence of Heat on the Strength of Iron. *Proc.* Inst. Civil Engrs. (1890–91) **104**, 209.

[5] F. N. Speller: Discussion on Recrystallization as a Factor in the Failure of Boiler Tubes. *Proc.* Amer. Soc. Test. Mat. (1916) Pt. 2, 112.

[6] F. C. Lea and O. H. Crowther: Change of the Modulus of Elasticity and of the Other Properties of Metals with Temperature. *Engng.* (1914) **98**, 487.

[7] C. Bach: Versuche über die Verschiedenheit der Elastizität von Fox-und Morison-Wellrohren. *Zeit. Ver. deut. Ing.* (1904) **48**, 1227; Versuche über die Festigkeit seigenschaften von Flusseisenblechen, etc. *Ibid.* (1904) **48**, 1342.

[8] J. E. Howard: Physical Properties of Iron and Steel at Higher Temperature. *Iron Age* (1890) **45**, 585.

[9] Zay Jeffries: *Trans.* (1919) **60**, 474.

[10] A. K. Huntington: Effect of Temperature on Tensile Tests of Copper and its Alloys. *Jnl.* Inst. Met. (1912) **8**, 126.

temperatures on wrought iron and mild steel, and although some of the points indicated at temperatures above the ordinary are higher than the room-temperature values, the curve that he draws does not pass through a maximum value. The decrease plotted by his own curve, however, is not in accordance with the decrease expected with an increase in temperature, but indicates a discontinuity. Recently, H. J. French, of the U. S. Bureau of Standards, has determined carefully the elastic limit as well as other tensile properties of mild steel and checks Martens' results; the elastic limit is about the same at 250° C. as at room temperature and it passes through a maximum value at 200° C. about 15 per cent. greater than that at room temperature. Epps and Jones report a 10 per cent. increase in wrought iron in the corresponding temperature range. Notwithstanding the report by Howard, in 1890, that the elastic limit of iron and steel decreases with a rise in temperature, the evidence to the effect that the elastic limit in iron and mild steel is greater at 200° C. than at room temperature is overwhelming. That this is true in medium- and high-carbon steels is not certain.

The elongation of iron and mild steel decreases above room temperature and passes through a minimum between 100° and 300° C. and then increases up to 500° C. The elongation at 500° C. is greater than that at room temperature. Epps and Jones report minima elongation values in wrought iron at 100° to 150° C. and 500° to 550° C. and a maximum at about 300° C.; this decrease above 300° C. does not seem to be the rule.

The reduction of area of iron and mild steel seems to increase at temperatures slightly above room temperature and then decreases, passing through a minimum about 300° C., and then increases up to about 500° C. Above 500° C., the elongation and reduction of area both vary markedly with grain size and the rate of loading. The effect of liquid-air temperature (about −190° C.) on iron and steel is greatly to increase the strength and decrease the ductility.[11]

Recovery of Elasticity of Iron and Steel after Overstrain

Prof. H. M. Howe has called attention to the fact[12] that recently deformed mild steel loses its elasticity. The effect of rest at room temperature is slowly to restore the elasticity and eventually to raise it above the load that caused the previous deformation. The effect of warming is greatly to hasten the recovery of elasticity. J. Muir,[13] in three papers, discusses in detail the elastic recovery of recently overstrained steel.

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[11] R. A. Hadfield: Alloys of Iron and Tungsten. *Jnl.* Iron and Steel Inst. (1903) **64**, 14.

[12] "Metallurgy of Steel," 212. N. Y., 1890.

[13] J. Muir: On the Overstraining of Iron. *Phil. Trans.* Roy. Soc. London (1900) **A193**, 1; *Ibid.*, **A196**, 1; *Proc.* Roy Soc. London (1906) **A77**, 277.

He reports that the recovery of elasticity at 100° C. is as pronounced after three or four minutes as in two weeks at room temperature. In the mild-steel samples with which he worked, he found no change in elastic properties in the material in its original state, after boiling in water or after heating to 250° C. After slightly deforming by tension, however, the material lost almost entirely its elasticity and recovered it very gradually, the complete recovery being effected in about two weeks. If the material is allowed to rest at a low temperature, say around 0° C., the recovery is much impeded or totally stopped.[14]

Muir found that steel containing about 0.2 per cent. carbon recently quenched from a red heat was imperfectly elastic when tested immediately, but when deformed in this state it immediately became perfectly elastic, up to the load that produced the deformation.

Effect of Permanent Deformation of Iron and Steel in the Blue-heat Range

As mentioned above, Stromeyer warns against the working of steel in the blue-heat range because it produces brittleness. Howe[15] calls attention to the fact that steel bent at blue heat is stronger than steel bent a like amount at ordinary temperature. Howard gives the following quantitative information on a steel containing 0.97 per cent. carbon; its elastic limit at room temperature was 82,000 lb. per sq. in. (5764 kg. per sq. cm.) and the tensile strength was 154,000 lb. per sq. in. (10,826 kg. per sq. cm.). When stressed to 140,000 lb. per sq. in. (9842 kg. per sq. cm.) at a temperature of 535° F. (279° C.) and broken at 70° F. three days later it showed an elastic limit of 164,000 lb. per sq. in. (11,529 kg. per sq. cm.) and a tensile strength of 167,000 lb. per sq. in. (11,740 kg. per sq. cm.). Its normal elastic limit at the temperature of deformation was 64,000 lb. per sq. in. (4499 kg. per sq. cm.).

The present author has made tests on blue-heat deformation of Armco iron and has compared the tensile properties both at ordinary and at elevated temperatures. The following conclusions are made from this work.

1. Armco iron deformed at room temperature a given amount does not increase as much in tensile strength as when deformed the same amount at blue heat.

2. When Armco iron is drawn cold, its tensile strength at 200° to 300° C. is greater than at room temperature with moderate reductions by drawing; but with 96 per cent. reduction of area by cold drawing, the tensile strength is greater at room temperature than at any higher tempera-

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[14] W. A. Scoble: Report on Combined Stress. Brit. Assn. for Adv. of Sci. (1913) Sec. G.

[15] *Op. cit.*, 234.

ture. The tensile strength-temperature curve, however, shows clearly that it passes through a change point inasmuch as the strength does not decrease as rapidly from 15° to 300° C. as from 300° up. The decrease in strength is also much more rapid from −190° C. (liquid-air temperature) to 15° than from 15° to 300° C.

3. The effect of drawing Armco iron wire at 200° to 400° C. is to produce greater tensile strength at all temperatures up to 550° C. than would result from the same amount of deformation in the cold. The elongation is less after drawing at 200° to 400° C. than after drawing the same amount at room temperature. The same conclusion is true in general of the reduction of area.

The results given by W. E. Ruder,[16] in Table 1, show the effect of rolling cold and at various elevated temperatures on the strength of mild steel. His results on a nickel-chromium steel in the annealed condition are given in Table 2.

TABLE 1.—*Effect of Rolling Hot and Cold on the Tensile Strength of Mild Steel*

	Ultimate Strength, Lb. per Sq. In.		Ultimate Strength, Lb. per Sq. In.
0.192 in. diameter	58,200	0.192 in. diameter	112,700
Annealed	55,200	Reduced to 0.179 in. at 300° C.	113,500
0.192 in. diameter	67,000		
Reduced to 0.179 in. cold	69,500	0.192 in. diameter	114,100
0.192 in diameter	110,200	Reduced to 0.179 in. at 400° C.	105,300
Reduced to 0.179 in. at 240° C.	112,300		

TABLE 2.—*Method of Treatment, Nickel-chromium Steel*

	Tensile Strength, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Per Cent. Elongation in 2 In.
Annealed	101,500	67,100	25.5
Annealed, then reduced 10 per cent. at 300° C.	137,600	132,500	10.5
Heat treated and reduced 10 per cent, at 300° C.	199,100	163,700	7.5
Annealed and reduced 10 per cent. cold	114,200	102,000	19.5

[16] Private communication, May 28, 1918.

Effect of Aging on Tensile Properties of Heat-treated Medium-carbon Steel

Reinhardt and Cutler[17] found that steels containing 0.35 to 0.45 per cent. carbon gave no trouble in obtaining the necessary physical properties when the samples were machined and tested immediately after heat treatment; but in steels containing carbon between 0.49 and 0.55 per cent., the tests taken from billets 5¾ in. (14.6 cm.) square showed inferior elongation and reduction of area if tested immediately after heat treatment and machining, whereas after resting at room temperature for even 12 to 24 hours the results were increased sometimes more than 100 per cent. Heating to 120° C. effected this increase more quickly than room-temperature aging. Test bars turned from ingots of steel having the same chemical composition rolled to 1⅞ in. square billets did not show the inferior values in elongation and reduction of area immediately after treatment. From the tabulated data given by Reinhardt and Cutler, it would seem that complete restoration of ductility takes place in about 25 hours at 120° C. and in about 16 days at room temperature. It should be noted that this aging effect is not associated with previous plastic deformation and, consequently, is a different phenomenon from the recovery of elasticity after overstrain. That aging was necessary to increase the ductility of forgings has been known, or at least suspected, for many years but the results given by Reinhardt and Cutler give unquestionable quantitative evidence on this subject.

Thermal Critical Points Below A_1

Cloup[18] reports an evolution of heat on rise of temperature in all steels that have previously undergone cold working or heat treatment. The point occurs at about 400° C. in all cases and is not reversible. Honda[19] reports that there is strong evidence of the existence of an allotropic point at 215° C. in steel, which is missing in pure iron, as is the A_1 point. He finds in cementite a marked magnetic transformation at 215° C., which is reversible. He finds the same point in steels containing 1.5, 1.02, 0.80, 0.64, and 0.18 per cent. carbon. The magnitude of the transformation decreases as the carbon content is lowered and is zero in pure iron. He also finds transformations at both 400° and 215° C. in annealed tungsten steel, indicating a transformation in another carbide at 400° C. Doctor

[17] G. A. Reinhardt and H. L. Cutler: Effect of Time and Low Temperature on Physical Properties of Medium-carbon Steel. *Trans.* (1920) **62**, 420.

[18] F. Cloup: Trempe et Ecrouissage des Aciers au Carbone. *Compt. Rend.* (1918) **166**, 415; *Jnl.* Amer. Soc. Mech. Engrs. (1918) **40**, 500.

[19] K. Honda: On Magnetic Analysis as a Means of Studying the Structure of Iron Alloys. *Jnl.* Iron and Steel Inst. (1918) **98**, 375.

Mathews[20] reports a thermal change in nickel-chromium steel below the A_1 point.

Surface Deformation in Steels Quenched from Blue Heat

Zschokke[21] found that on heating a square gage of steel to a temperature between 225° and 400° C. and quenching in water, the polished face became plaited or folded so that the markings could be observed macroscopically. Bogitch[22] has studied this phenomenon more completely. The formation of this folding on the polished surfaces of steel depends on several factors, as follows:

1. Quenching in boiling water does not deform the polished surface. On the other hand, on quenching in iced water or salt water at −18° C. the range of folding is slightly widened.

2. At each quenching temperature, a definite type of marking or folding is obtained if the conditions of quenching mentioned are adhered to. For each quenching temperature all the types of markings corresponding to lower temperatures may be obtained by diminishing the duration of heating.

3. The piece of steel once quenched loses, at least partly, its ability to form these markings or foldings. It is necessary to anneal above 700° C. to cause it to regain this property.

4. When progressively smaller gages of the same thickness are quenched, the quenching temperature range within which the folds are observed diminishes until it disappears with the gage 1 cm. on a side.

Thermal and Electrical Conductivities of Iron and Steel

Two papers by Honda and Simidu,[23] on the thermal and electrical conductivities of carbon steels at high temperatures, show an irregular change in the heat conductivities of carbon steels containing from 0.18 to 1.5 per cent. carbon. The decrease in conductivity is not marked until a temperature near 300° to 400° C. is reached, after which it decreases quite rapidly with temperature. The thermal conductivity of Swedish iron decreases more uniformly from room temperature to 500° C., but one point lies off the smooth curve at the temperature of 234° C. The steel containing 1.02 per cent. carbon actually has higher thermal conductivity at 250° C. than at room temperature and several of the readings in the tow-temperature range do not lie on a smooth continuous curve.

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[20] Private communication.

[21] B. Zschokke: L'influence des Brusques Changements de Température sur l'acier Doux. *Rev. de Met., Mem.* (1910) **7**, 165.

[22] B. Bogitch: Sur les Déformations Superficielles des Aciers Trempés aux Température peu Élevées. *Compt. Rend.* (1915) **160**, 768.

[23] K. Honda Takeo Simidu: *Sci. Repts.*, Tokohu Univ.

TABLE 3.—*Analyses of Steels*

	Steel			
	H57	C4	C5	C7
Carbon, per cent	0.57	0.76	0.945	1.05
Manganese, per cent	0.11	0.221	0.189	0.190
Phosphorus, per cent	0.010	0.016	0.013	0.013
Sulfur, per cent	0.020	0.041	0.016	0.020
Silicon, per cent	0.17	0.169	0.155	0.167

TABLE 4.—*Effect of Tempering on Specific Resistivity*

	Steel			
	H57	C4	C5	C7
Carbon, per cent	0.57	0.76	0.945	1.05
Specific resistivity:				
When quenched from 907° C	21.88	32.24	36.32	39.73
On tempering 1 hr. at 100° C. to 108° C	20.67	27.47	29.62	32.97
On tempering 1 add. hr. at 100 C. to 108° C.	20.54	27.47	29.12	32.18
On tempering 1 add. hr. at 100° C. to 108° C.	20.54	27.07	28.89	31.58
On tempering 3 add. hr. at 100° C. to 108° C.	20.27	26.55	28.27	30.32
On tempering 6 add. hr. at 100° C. to 108° C.	19.87	25.75	27.31	29.19
Total drop in 12 hr. tempering	2.01	6.50	9.01	10.54

TABLE 5.—*Effect of Aging on Resistivity*

	Steel			
	H57	C4	C5	C7
Carbon, per cent	0.57	0.76	0.945	1.05
Specific resistivity when quenched from 906° C	21.07	32.64	35.85	40.00
After standing 7 days at room temperature	21.17	32.48	38.53	39.87
After 14 days	21.21	32.45	35.50	39.80
After 21 days	21.11	32.31	35.22	39.67
After 28 days	21.17	32.24	35.12	39.33
After 2 months	21.01	31.78	34.50	38.99
After 3 months	20.94	31.18	34.10	38.32
After 4 months	20.84	31.05	33.70	37.76
After 6 months	20.94	31.02	33.70	37.76
After 9 months	20.82	30.71	33.24	37.27
After 12 months	20.87	30.83	33.24	37.27
After 18 months	20.87	30.55	32.87	
After 24 months	20.60	30.33	32.53	36.47
Total drop in specific resistivity in 24 months at room temperature	0.47	2.31	3.32	3.53

The electrical resistivities of Swedish iron and carbon steel show smooth curves with uniform slope with the exception of steels containing 1.02 per cent. and 1.3 per cent. carbon, which have points lying off the smooth curves in the temperature range 175° to 275° C. Meyer[24] gives electrical-resistivity curves of pure iron showing slight discontinuities in the blue-heat range. Prof. E. D. Campbell[25] shows that the electrical resistivity of hardened steel decreases with rest at ordinary temperatures and much more rapidly at 100° C. Tables 3, 4, and 5 give the complete data on his experiments.

Curves are shown in the original paper. The change of electrical resistivity at ordinary temperatures after two years is only from about 35 per cent. to a little more than 40 per cent. of that produced in 12 hours at 100° C. The work of Barus and Strouhal[26] shows that with a rise of temperature above 100° C., the rate of decrease of electrical resistivity is much accelerated.

Spontaneous Generation of Heat and Spontaneous Contraction in Recently Hardened Steel

When J. E. Howard[27] attempted to determine the coefficient of expansion of hardened high-carbon steel, he found an abnormally low result, which was explained after remeasuring the length at the low temperature. It was found that the steel had permanently contracted in length and obviously the rise in temperature had greatly hastened this change in volume. Charles F. Brush[28] reports the spontaneous generation of heat and spontaneous contraction in recently hardened high-carbon steel and high-speed steel at room temperature. In Brush's first experiments, an evolution of heat only was noted and the apparatus he devised was so sensitive that the heat evolution could still be detected after 5 weeks. Later experiments on a nickel-chromium steel, furnished by Sir Robert Hadfield, showed a spontaneous absorption of heat if quenched during the rise of temperature between 530° and 667° C., but an evolution of heat if quenched on falling temperature. These results are all summarized together, with additional data in a paper by Brush, Hadfield and Main.[29] The conclusion is drawn that the heat evolved in the high-carbon and high-speed steels is far in excess of that due to the contraction

[24] A. R. Meyer: *Ber. deut. phys. Gesell.* (1911) **9**, 680.

[25] E. D. Campbell: On the Rate of Change at 100° C. and at Ordinary Temperatures in the Electrical Resistance of Hardened Steel. *Jnl.* Iron and Steel Inst. (1918) **98**, 421.

[26] C. Barus and V. Strouhal: Electrical and Magnetic Properties of Iron Carburets. U. S. Geol. Survey *Bull.* 14 (1885).

[27] *Iron Age* (1890) **45**, 585.

[28] C. F. Brush: Spontaneous Generation of Heat in Recently Hardened Steel. *Proc* Amer. Phil. Soc. (1915) **54**, 154; *Phys. Rev.* N. S. (1917) **9**, 228; *Proc.* Amer. Phil. Soc. (1917) **56**, 353.

[29] Brush, Hadfield and Main: *Proc.* Roy. Soc. London (1918) **A95**, 120.

alone. The rate of contraction in recently hardened steel is increased by heating and the magnitude is also affected.

Effect of Quenching Nickel-chromium Steels on Resistance to Impact

The Midvale Steel Co. has, for several years, known that certain nickel-chromium steels have low resistance to impact when cooled slowly from the tempering heat (about 600° C.) but if quenched from the tempering heat the impact values are satisfactory. Philpot[30] gives many impact results on nickel-chromium steels showing the increased resistance produced by quenching from the tempering heat. This property in nickel-chromium steels is known as "blue brittleness." All steels of this class do not show the phenomenon of blue brittleness; it seems to be more pronounced in acid than in basic steel. The ratio between the impact values of the steel quenched from the tempering heat and that cooled slowly from the tempering heat may be considered as a rough measure of the susceptibility to blue brittleness. Some steels cooled slowly from the tempering heat show a higher impact resistance than when quenched from this temperature. Of one series of 20 tests, three showed higher impact values after slow cooling and 17 showed higher values after quenching. The ratio of impact resistance after quenching to that after slow cooling from the tempering heat varied from a little less than unity to 13. The general type of steel considered is typified by the following analysis: carbon, 0.40 per cent.; nickel, 2.75 per cent.; chromium, 0.85 per cent.; manganese, 0.8 per cent.; sulfur, 0.035 per cent.; phosphorus, 0.025 per cent.

A steel susceptible to blue brittleness that has been made resistant to impact by quenching can have its impact value reduced by heating to temperatures between 750° and 1020° F. (400° and 555° C.) regardless of the manner of cooling from these temperatures. A piece of steel originally having a low impact resistance produced by slow cooling from the tempering heat may have its impact value restored to normal by heating to about 1100° F. (593° C.) and quenching. Steel exhibiting the phenomenon of blue brittleness will, if tempered at consecutively higher temperatures beginning at 200° F., show brittleness between 400° and 1000° F., regardless of the manner of cooling from the tempering heat, but at 1100° F. the high resistance to impact can be restored.

Some interesting conclusions are drawn from results reported by Capt. H. F. Wood and R. S. Archer.[31] The steels used contained: carbon, 0.3 to 0.4 per cent.; manganese, 0.5 to 0.6 per cent.; nickel, 2.75 to 3.15 per cent.; chromium, 0.75 to 0.85 per cent.; sulfur, less than 0.031

[30] H. T. Philpot: Some Experiments on Notched Bars. *Jnl.* Soc. Automot. Engrs. (1918) **3**, 347.

[31] Report to Committee on Physical Changes in Iron and Steel below the Thermal Critical Range (Jan. 3, 1919).

per cent.; phosphorus, less than 0.035 per cent.; silicon, less than 0.14 per cent. A certain steel was tested to make sure of its susceptibility to blue brittleness and was heated to 1670° F. (910° C.) and air-cooled, then heated to 1510° F., held one hour and quenched in oil, and finally several samples were heated to 1100° to 1125° F., for one-half hour and cooled, as here shown. The impact values are higher as the time of cooling to room temperature decreases.

Manner of Cooling	Izod Impact Values
Water quenched	50.0
Oil quenched	48.0
Air cooled	43.0
Furnace cooled	8.7

A piece of steel susceptible to blue brittleness that has been made resistant to impact by quenching from the tempering heat cannot be made brittle by heating quickly to a temperature of 950° F. (510° C.). This shows that appreciable time is required for the internal changes that cause the low impact values after the steel has cooled to take place at 950° F. On the other hand, a very short exposure at 1100° F. (595° C.) is sufficient to restore the impact resistance of a steel made brittle by previous slow cooling through the temperature range below 1100° F.

Wood and Archer describe experiments showing that a nickel-chromium steel susceptible to blue brittleness had a lower impact value when annealed and slowly cooled from 1100° F. than when the annealed steel was quenched from 1100° F. The brittleness developed is, therefore, inherent in the steel irrespective of the heat treatment previous to tempering.

Archer[32] has shown, beyond question, that the impact fracture of certain of these steels after slow cooling from the tempering heat is intercrystalline. When the fracture is known to be intercrystalline the macroscopic appearance is described as "crystalline." On the other hand, it is certain that the fracture of the specimens showing high impact values is transcrystalline; in such a sample the appearance of the fracture is fibrous. Wood and Archer describe the fractures of specimens having intermediate impact values as partly crystalline and partly fibrous and have estimated roughly the percentage of each on certain fractures and have compared them to the impact values. These results are given in Table 6.

It appears that the cause of blue brittleness relates to changes tending to produce intercrystalline fracture and, consequently, the appearance of the fracture after impact test should be an indication of the impact resistance. It also appears that the grains are as deformable, or nearly so, in the samples showing low impact values as in those showing high values. The grain boundaries in the former become so weak that sufficient load

[32] R. S. Archer: Development of Grain Boundaries in Heat-treated Alloy Steels. *Trans.* (1920) **62**, 754.

to deform the grains themselves cannot be applied quickly without pulling them apart. The grains here referred to are, in outline, the old austenite grains although the heat treatment must have changed the

TABLE 6

Treatment of Steel	Impact Test, Foot-pounds	Approximate Per Cent. of Fractured Surface Appearing Crystalline	Treatment of Steel	Impact Test, Foot-pounds	Approximate Per Cent. of Fractured Surface Appearing Crystalline
Annealed	4.0	100	Annealed	36.0	60
Annealed	8.0	100	Annealed	42.5	20
Annealed	8.0	100	Annealed	47.5	20
Annealed	13.0	80	Hardened	26.0	50
Annealed	16.0	70	Hardened	33.0	40
Annealed	17.0	70	Hardened	48.5	0
Annealed	33.5	60	Hardened	52.0	0

interior from austenite to sorbite. One of the unusual characteristics of these steels is the persistence of the austenite grain boundaries after heat treatment.

The tensile properties of these steels showing low impact values are approximately the same as those showing high values. The blue-brittleness tendency is, therefore, not detected by the tensile tests. Precautions against blue brittleness advised by Wood and Archer are as follows: Temper above 1020° F. (550° C).; quench from the tempering heat; avoid reheating any specimen to temperatures between 750° and 1020° F. (440–550° C.).

It is not certain that the steels having low impact values, provided the tensile properties are good, are unfit for use for aircraft-engine crankshafts or for similar purposes. It is considered safer, however, at the present time, to treat for a high impact value.

GENERAL DISCUSSION

The changes in the tensile properties of iron and steel with a rise in temperature are best explained by assuming a low-temperature allotrope in iron. Since all of the tensile properties change gradually with a rise in temperature rather than abruptly at a given temperature, the change from one allotrope to another would be considered to take place gradually. The point of maximum tensile strength need not be considered as the temperature at which the allotropic change on heating has been completed, but it would seem that the change takes place gradually between ordinary temperature and about 350° C. The temperature of maximum strength might well correspond to the physical state of the metal in which both allotropes are present in about equal proportions. The difficulty of explaining the tensile properties of iron at elevated temperatures with-

out assuming the existence of an additional low-temperature allotrope seems to the writer almost unsurmountable. The changes in tensile strength and elastic limit are opposite to those normally expected by increase in temperature. The magnitude of these changes of properties is such as to leave no doubt as to the existence of a maximum point in tensile strength and elastic limit at about 200° to 250° C. Iron possesses considerable ductility throughout the entire temperature range within which these physical changes take place. The phenomenon cannot, therefore, be attributed to a change from a brittle to a ductile condition, or vice versa. Furthermore, the fracture of iron from room temperature to 500° C. takes place through the grains rather than at the grain boundaries. This suggests that internal changes have taken place within the grains, other than those changes ordinarily produced by change in temperature alone. These grains are composed of crystalline material. If a change within the grains of this crystalline material takes place between room temperature and 500° F., why not call this an allotropic change? We have no other name for such a change at present. It should not be necessary for one allotrope to change to another at a specific temperature. The change might well take place at a particular temperature in the higher temperature ranges, such as at the A_3 point in pure iron, but at the low temperatures with high mechanical cohesion to resist allotropic change we might expect the transformation to be more sluggish. If there is a low-temperature allotrope in iron, the grains we examine under the microscope at room temperature are pseudomorphs of the grains formed originally when the iron was in another allotropic state. The temperature of the lower change is too low to permit a general recrystallization like that at A_3.

It is assumed that allotropy can occur only in a crystalline phase and that amorphous metal exists between the grains of crystalline metal and is generated within the grains during plastic deformation. All of the results produced by cold deformation, as well as blue deformation reported above, accord nicely with the theory of the existence of a low-temperature allotrope in iron. We would expect the amorphous phase to change continuously with temperature and become weaker at 200° to 300° C. than at room temperature. In order that the elastic limit of iron may be higher at 200° C. than at room temperature, the crystalline grains must have their elastic limit increased by increase in temperature. Since the tensile properties are functions of the quantity, arrangement, and properties of the amorphous and crystalline phases of iron, the greater amount of amorphous metal in severely cold-drawn iron wire produces less increase in strength at elevated temperatures than does the smaller amount of amorphous metal in annealed iron. Since the amorphous phase decreases in strength continuously with temperature, the Armco iron reduced by cold drawing 96 per cent. of its original area was not stronger at any elevated temperature than at ordinary temperature.

Since the crystalline phase of this same sample had increased in cohesion at the elevated temperatures, the tensile strength of even this severely deformed iron did not decrease at a regular rate with a rise in temperature; it decreased in strength but slightly up to 250° to 300° C., after which an additional increase in temperature produced a marked decrease in the tensile strength.

The failure to discover sharp changes in thermal and electrical conductivities of iron and steel with a rise in temperature is not necessarily evidence against the existence of a low-temperature allotrope in iron. The change from one allotrope to another throughout a temperature range of 300° or more might mask any sharp change in these properties.

The explanation of some of the aging results described above is at the present time very problematical. It is certain that atomic rearrangements of considerable magnitude take place in iron and steel at room temperature. The mechanical cohesion resists these atomic changes so that the time effect is very pronounced. For example, the spontaneous generation of heat in recently hardened steel which releases itself gradually during a period of five weeks or more is released quickly at an elevated temperature. Nearly all of the aging results, however, indicate an equilibrium condition of the metal reached after a long period at room temperature or a short period at 100° C. Still higher temperatures may produce internal changes not reached in room-temperature aging.

The nature of these internal atomic changes may be either chemical or physical. In the elastic recovery of overstrained iron, for example, the internal changes would seem to be of the nature of the establishment of cohesion bonds between the atoms of the amorphous metal newly formed by the deformation. This gives rise to the speculation as to whether the establishment of cohesion bonds would generate heat in proportion to the latent heat of evaporation. Recently overstrained steel should be examined for spontaneous generation of heat and for spontaneous change of volume.

Having taken the stand that the tensile and deformational properties of iron and steel could not be explained without assuming the existence of a low-temperature allotrope, let us see if this assumption also assists in the explanation of some of the other observations noted.

The formation of folds[33] would indicate a volume change from one allotrope to another and also would indicate that the rate of change from one allotrope to another is so slow that quenching prevents the transformation from taking place during cooling but allows it to take place at the temperature of the quenching bath. The fact that a small piece will not develop these folds would indicate that the effect is cumulative in a large piece and may not reach sufficient magnitude in a piece of 1 cm. square to cause the initiation of the folding.

[33] B. Bogitch: *Op. cit.*

It is reported that quenching alone from blue heat affects the properties of steel. This can be explained readily by assuming a low-temperature allotrope.

The spontaneous generation of heat, the contraction, and the decrease in electrical resistivity at ordinary and slightly elevated temperatures in hardened and untempered high-carbon steels are probably results of the same internal changes. These changes are produced in a few minutes in hardened tool steels by tempering between 175° and 300° C. If we did not suspect the existence of a low-temperature allotrope, we would attribute these changes to the normal tendency of martensite to change toward troostite; but because of the strong evidence of the actual existence of such an allotrope, we are tempted to attribute at least part of the changes to it. The greatly increased hardness due to the carbon and quenching might retard the transformation of the low-temperature allotrope to such an extent that the change is incomplete with rapid cooling through this range. The completion of the transformation would take place slowly at room temperature and more rapidly at 100° C.

Blue brittleness in nickel-chromium steels seems to involve relative changes in properties of the grain-boundary material and the grain material. This relative change might be caused by differential volume changes in the two materials, due to different rates of cooling from the various temperatures; or there may be an actual precipitation on cooling and absorption on heating of excess material at the grain boundaries, the rapid cooling from the higher tempering heats preventing the precipitation. The thermal point below A_1 reported by Doctor Mathews would indicate some condition like the latter. This is complicated by the presence of nickel and chromium, especially the former, which has such peculiar effects on steel when present in large amounts.

A rather comprehensive investigation of blue brittleness in various steels is in progress by some members of the committee, namely, Miller, Mathews, Wood, Nelson, and Foley.

In the interpretation of all of these changes in properties of iron and steel at low temperatures, we have to consider the question of internal strain. The modern diagnosis for unusual metal ills is "internal strain." That these strains exist is not doubted; but we call ailments of all kinds and magnitudes and due to different causes, internal strains. We may have internal strains between like atoms, between atoms of two or more elements, between groups of like atoms or unlike atoms; these may be either chemical or physical strains. We have also regional internal strains of as many varieties as we have external stresses. To say simply that a metal is afflicted with internal strains is the same as saying that a patient is sick without consideration of the cause or remedy.

Take, for example, the spontaneous contraction in recently hardened steel reported by Brush; did the diameter of the small rod that he used

contract in proportion to the contraction in length? Let us assume that it did. If we consider that the contraction was due to internal strains, we could bring the rod back to its original length by applying simple tension; but, in accordance with Poissan's ratio, this would actually decrease the diameter. The only way we could restore the shape to the original one would be by applying negative hydrostatic pressure, and it is obvious that this would not restore the atoms to their original positions. Such internal strains would be very complex. The rod used by Brush was so small that it must have hardened to its axis. When a large block of high-carbon steel, like a forging die, is quenched, however, only the outside shell is changed to martensite, and several degrees of hardness exist between the shell and the interior parts. We can imagine these layers of different hardness having different magnitudes of spontaneous contraction; rest at room temperature might thus cause such an increase in internal strains that the shell would rupture or crack. This spontaneous cracking of large die blocks is common and the remedy is to allow as little time as possible beween the quench and the draw and in some cases, to insure against such cracks, the quenching water should be hot.

Owing to the uncertainty as to the nature of martensite, troosite, etc., and the possibilities for both physical and chemical changes, the explanations of the observations discussed in this paper must await additional data. The following points would make excellent subjects for research at colleges and universities and research laboratories in the steel industry:

1. Is there a difference in volume between samples of a steel quenched from 200° to 400° C. and one slowly cooled from this range? Is there a change in physical properties?

2. Does recently overstrained iron and steel generate heat at room temperature? Is there a volume change corresponding to the recovery of elasticity?

3. Is the spontaneous contraction in recently hardened steel uniform or directional?

4. How can we establish the existence or non-existence of the low-temperature allotrope in iron beyond reasonable doubt?

5. What are the deformational characteristics of low-carbon martensite at ordinary temperature and at blue heat? Also the tensile properties?

No doubt much information is extant that would help to answer some of these questions and if so it is hoped that it will be offered in discussion.

Practical Value of Work in this Field

The question of hot straightening of warped forgings is important; and if straightening bent forgings at a blue heat is detrimental, this fact should be known. It is also conceivable that the variations in properties

of iron and steel produced by blue-heat deformation might be taken advantage of for useful purposes in the future.

The old-time practice of tempering high-carbon steel at temperatures so low that no appreciable change in hardness occurs is seen, from the above descriptions, to have good scientific foundation. The slow changes in volume at room temperature may even produce cracks in high-carbon steels quenched but not tempered. This is so pronounced in certain large pieces that the tempering must follow the quenching almost immediately, to avoid the formation of so-called quenching cracks. In certain steels, quenching in hot water and oil are resorted to because cold-water quenching might produce these cracks before the steel could be removed from the bath or even during cooling.

Rosenhain and Archbutt[34] report the formation of intercrystalline cracks that, eventually, produce failure in mild-steel boiler plates. These boiler plates are used at a relatively high temperature and it is the belief of the authors that the long-sustained load at the high temperatures causes the amorphous cement at the grain boundaries gradually to flow and eventually break without deformation of the grains. This involves the study of the action of steel under sustained loads at elevated temperature, which subject is now being investigated by H. J. French at the Bureau of Standards. Epps and Jones state that the elastic limit of wrought iron at 600° F. (315° C). is only half that at room temperature; hence in designing tubes, valves, pipe lines, etc., for carrying superheated steam, a safety factor of 10 should be used on the basis of the tensile strength at room temperature. This would represent a factor of safety of 3 on the elastic limit at 600° F.

Quenching nickel-chromium steels from the tempering heat is resorted to in many cases to increase the resistance to impact. While there may be criticisms to the effect that the high impact values so produced are unnecessary, there seems to be no contention that such steel is inferior to that which has been slowly cooled.

In conclusion, it may be stated that information on all of the subjects treated in this paper will help, either directly or indirectly, in the production, treatment, and control of iron and steel with properties more suitable to the uses of mankind.

DISCUSSION

F. C. LANGENBERG,* Watertown, Mass. (written discussion).—Doctor Jeffries is to be congratulated on the thoroughness with which he has reviewed the various peculiar physical properties which occur in iron and steel at low temperatures, but I seriously question whether it is

[34] Rosenhain and Archbutt: *Proc.* Roy. Soc. London (1919) **A96**, 55.

* Metallurgist, Watertown Arsenal.

either right or necessary to attribute all of these peculiar properties to a low allotrope. It has been known at this arsenal for several years that certain nickel-chrome steels were susceptible to a brittleness when slowly cooled from the tempering heat; it was never felt, however, that this brittleness was in any way connected with what is commonly known as "blue brittleness."

A paper is now in preparation by the writer of this discussion which offers certain evidence showing that "blue brittleness" is a distinctive property of free ferrite, and furthermore, that blue brittleness is not a property of free ferrite at a blue heat, but rather is a property resulting from a mechanical deformation of free ferrite at a blue heat or lower temperatures. In so far as this property has been studied in the laboratory at Watertown arsenal, the idea of a new allotrope is not necessary to explain the physical properties observed.

Doctor Hemingway and Mr. Ensminger, of this laboratory, are now carrying out certain investigations on nickel-chrome steels that exhibit brittleness after slow cooling from the tempering heats. It would appear that in certain nickel-chrome steels there is a low critical change which is not due to ferrite, but is caused by either chromium carbide or, possibly, by some of the double carbides said to exist in these alloy steels. Honda has already shown that the carbide of iron undergoes a magnetic change at 240°C. and that also the double carbide of tungsten and iron shows a similar change at 400°C. Along the line of this work, it is believed that nickel-chrome steels may also form a carbide which has one of these low critical changes.

R. S. Archer,* Cleveland, Ohio.—Like Doctor Langenberg, I object to assuming an additional allotrope in iron if it can be avoided. According to our present notions, allotropy consists in the change in atomic arrangement. All the types of arrangement that we find in metals are simple. There is evidence that iron exists in two or perhaps three allotropic forms, that is, there are three different arrangements of iron atoms. It seems to me that the number of these simple arrangements is rather limited and that we should attempt to explain these facts without assuming allotropy, if possible.

I have worked out an explanation which depends on the fact that elastic recovery after overstrain is an action that takes time. Suppose that a ferrite crystal is deformed to the extent of producing one slip band, that is, that deformation takes place along one cleavage plane and that the deformation increases until the outside shape of the grain has changed a certain definite amount. Actually, such deformation would take place on a large number of slip bands and the change in the exterior shape of the grain would be gradual.

* Metallographist, Aluminum Manufactures, Inc.

When slip starts on the cleavage plane at room temperature, the mobility is great. Motion along this plane takes place easily, as we know. If after this slip has started we let iron rest for a few weeks at ordinary temperatures, or for a few hours at 100° C., or for a short time, possibly measured in seconds, at 200° or 300° C., this slip plane will have hardened so that the resistance to deformation along that plane becomes greater than the resistance to the formation of new slip planes.

Suppose that after slip takes place to a very small extent, an extent measured perhaps in atomic distances, the resistance to motion along this slip plane becomes great in a very short time. This probably occurs when the deformation is carried out at a temperature of about 300° C where the effects of overstrain are removed almost instantaneously. The slip, or cleavage, plane immediately develops a hardness greater than the crystalline and a new slip plane is formed, so that we have the same total deformation of the grain and the same exterior grain shape as was obtained with room-temperature deformation, but we have produced an enormously greater amount of amorphous material. As it is this amorphous material that produces grain hardening, that seems to be why greater hardening is obtained when deformation is carried out at higher temperatures. During the tensile test the same action is brought into play and, if the temperature is high enough to allow elastic recovery during the progress of the test, should raise the tensile strength. Whether this fact explains the increase in proportional limit, it is hard to tell. This theory also accounts for the decreased workability at a blue heat. The limit of deformation is reached sooner because more amorphous material is formed for a given deformation.

Doctor Jeffries has called attention to some objections to this explanation, the chief of which is that similar effects are not found in other metals. We should remember that such effects have not been looked for in other metals and that they may be found. Also, a critical condition is required in order that the mechanism here described may produce an increase in tensile strength with an increase in temperature. It is necessary that the effect of elastic recovery shall be greater than the normal effect of temperature in decreasing cohesion. It may be that this condition is of rare occurrence. In the case of metals in which this condition does not occur, there should be a discontinuity in the temperature-strength curve corresponding to an acceleration in the loss of tensile strength at temperatures somewhat below the temperature of recrystallization. We must also recognize the fact that the phenomenon of elastic recovery after overstrain is more pronounced in iron than in other metals.

E. F. KENNEY, Philadelphia, Pa.—Were the impact tests on this material that showed these wide divergences made at atmospheric temperatures or at blue heat?

ZAY JEFFRIES.—At atmospheric temperature.

E. F. KENNEY.—Then why the assumption that they are evidences of blue brittleness? Have you any other evidence that this is a phenomenon of blue brittleness?

F. N. SPELLER,* Pittsburgh, Pa.—The change in resistance to impact in soft steel that for some time has been repeatedly stressed inside the elastic limit has not been referred to among the internal changes produced below the critical temperatures. As this is one of the most common causes of failure of iron or steel in service, I call attention to this apparent omission, for there is much yet to be learned on this phase of the subject.

The breaking of an 8-in. wrought-iron pipe after 30 years service, the other day, resulted in considerable damage and loss of oil. The fracture, 5/16 in. thick, showed only three or four bright cleavage planes and not a sign of the fibrous appearance which usually characterizes the fracture of this metal. I have seen the same thing develop in boiler tubes, even where there was no apparent strain except that due to changes in temperature.

T. D. YENSEN,† East Pittsburgh, Pa.—There is one phenomenon that Doctor Jeffries has not mentioned; it occurs very slowly at room temperature and very much faster at 100°, and occurs in mild steels and pure irons; this is magnetic aging.

Magnetic aging is especially troublesome in magnetic apparatus, and one reason why silicon steel is used instead of pure iron is that the silicon takes care of the magnetic aging. Four per cent. silicon steel is practically non-aging. I have wondered if there is not some connection between the phenomena that Doctor Jeffries has described and magnetic aging.

W. E. RUDER,‡ Schenectady, N. Y.—The question of magnetic aging is, undoubtedly, tied up with these other low-temperature phenomena. We have considered it; but like a lot of other things, we have obtained no satisfactory information. Magnetic aging has, for a long time, been one of the unsolved mysteries in metallurgy to those who are interested in magnetism.

Some time ago, I conducted quite a long series of experiments, with the view to determining the cause of magnetic aging, that gave practically negative results. The thing was elusive, and the only clue that I had as to its cause was the fact that an anneal of low-carbon steels in certain gases almost entirely eliminated it. This formed the foundation for a theory I have been trying to build to fit the facts that Doctor Jeffries has

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† Research Engineer, Westinghouse Elec. & Mfg. Co.
‡ Metallurgist, General Elec. Co.

brought out in this paper, but like several of the other theories that have been mentioned today, including the one that Doctor Jeffries tentatively put forth, it does not answer all the facts. It was for this reason that I had no intention of bringing this one out at this time.

However, I do not believe that it is necessary for us to try to explain all of these phenomena by one theory, or by one set of assumptions. It is possible that several factors enter into them. It would be desirable if we could answer all in one broad way, but I do not think that our inability to do so should discourage us from trying to solve these mysterious changes that have just been outlined.

T. D. YENSEN.—Mr. Ruder made the interesting statement that magnetic aging in low-carbon steel can be largely eliminated by annealing in certain gases. If this is so, the other phenomena should also be subject to elimination by similar annealing. Furthermore, because of the fact that silicon added to iron also eliminates aging, it is very tempting to draw the conclusion that magnetic aging is due to oxides, and that perhaps all of the phenomena mentioned by Doctor Jeffries, may be due to the same cause. While the writer thinks that the phenomena are due, in part at least, to other causes, among which may be included the low-temperature allotrope, it may be well to keep the question of oxides in mind in the further investigation of these phenomena.

S. L. HOYT, Cleveland, Ohio.—If there is a low-temperature allotrope, we are justified in supposing it possible for the low-temperature allotrope to change into the high-temperature allotrope on heating; and, on cooling, for the high-temperature allotrope to change into the low-temperature allotrope. If that is true, we can examine the phenomenon from the point of view of the phase rule, in conjunction with the phenomena of allotropic or polymorphic transformations. Naturally at this temperature, with what we might call molecular sluggishness, we possibly would never get a definite stable equilibrium.

On heating and on cooling, we must exceed the equilibrium temperature before the transformation commences; that is why, a year ago, I suggested that the measurements of the physical properties be taken on falling as well as on rising temperature, so as to get a check on the hysteresis requirement. Secondly, if a true simple allotropic transformation takes place in iron, it would be quite natural to expect that all the properties would begin to show transformations at the same temperature, which would be higher on heating than on cooling. We have here certain tests that can be applied to allotropic transformations; I would like to see work of that kind done.

I had occasion, recently, to go over some thermal expansion curves of Drieser and to calculate the coefficient of expansion at both low and high temperatures. This work relates to the straight carbon steels. As

I recall, on running along the curves to pick out about a 200° temperature interval for the purpose of calculating the coefficient, there was a slight break at about blue heat.

There has been a question in my mind, in reading the paper under discussion, as to what is meant by the expression blue brittleness. The following is offered as a description of the phenomenon which I understand to be meant by the expression and I would appreciate learning how it agrees with the authors' definition. If a piece of material, with a hole in it like boiler plate with a rivet hole, is heated up to, say, 400° or 500° C. and allowed to cool to a blue heat, and a tapered mandrel is driven through the hole, so that the hole is enlarged in diameter, the material will split. This I have called "blue brittleness." If the tapered mandrel is driven through another plate similarly treated at room temperature, the material will not split. Just what relation that phenomenon has to the so-called blue brittleness of chrome-nickel steels, I cannot say.

ZAY JEFFRIES.—The term "blue brittleness" in connection with nickel-chromium steels is simply our translation for the original German term "Krupp-Krankheit," which this phenomenon was called. In the text of the paper there is no suggestion that that phenomenon in nickel-chromium steels is in the slightest way associated with the presence of a low-temperature allotrope; also there is no suggestion that the possible existence of a low-temperature allotrope is a panacea for all ills. I have suggested that if we assume the allotrope, some of these other changes would be bound to be modified by it. The only set of properties that I take a definite stand on, in the paper, are the tensile properties, and, as Mr. Archer has pointed out, those properties are as pronounced, or practically so, in pure iron as they are in steel. So that we have to leave out of consideration carbide changes and possible solution variations, and so forth, in order to account for those great changes. The statement about the so-called blue brittleness, or "Krupp-Krankheit" in the nickel-chromium steels, would also answer Mr. Kenney's question.

I do not consider that this brittleness in the nickel-chromium steels has necessarily anything to do with the other types of blue brittleness that we have discussed, and it is so considered in the text.

I should like to mention a possible theory for the blue brittleness, which was suggested by Radcliffe Furness. When I first talked with him about this subject, he stated that the ferrite had a tendency to separate out at the grain boundaries, at temperatures above the lower critical; he thought that the tendency might be there at temperatures below the lower critical, with ferrite dispersed throughout the matrix of sorbite. It is a fact that the ductility of the mass as a whole may not have any relation to the ductility of a certain constituent, even though it be in a

commanding position. Ferrite is perfectly ductile, and we might suspect that ferrite at the grain boundaries would promote ductility, but we must remember that the grains themselves are no longer the soft and easily deformable ferrite, but they are relatively hard, strong sorbite. So if we should surround these sorbite grains with thin films of ferrite, even though that ferrite is in large masses and, taken by itself, very ductile, it is also quite weak; so that in a tensile test, it is easily conceivable that a thin film of ferrite would break at a load lower than the elastic limit of the sorbite grains.

Mr. Archer's theory is plausible. It is a modification of the theory that is quite generally accepted in connection with nearly all metals now, that when deformed at ordinary temperatures and then heated to temperatures just below the first recrystallization, there is a slight hardening effect. An increase in tensile strength is noted in brass and aluminum and other metals. No other metal, however, has, so far as present results go, given anything like the quantitative variations that iron does. Mr. Sykes is now working on nickel.

While I do not share Mr. Speller's belief that there may be changes in the crystal orientation due to the time, or for long periods in which the metal is under stress, the general effect of repeated stress in long time is to produce a few slip bands and finally failure. The mechanism of breakdown is one of a local irreversible deformation. That is, when we bend a bar a little, we introduce so much cold work. When we straighten it again, we do not subtract that cold work and produce annealed iron, but we get twice as much work into it as we had after the first bending, and so forth. So those internal changes are irreversible, that is, accumulative, and I imagine that 30 years of cumulative changes of that nature might produce failure, but I should think the failure would be of the ordinary fatigue failure type.

It is assumed, as a general thing, that every property of steel changes at ordinary temperatures, with these changes mentioned. For example, we would not anticipate that a piece of steel could reduce its volume and give out heat or change its electrical resistivity, without changing every property a certain amount.

Doctor Hoyt's suggestion of taking the curves on both rising and falling temperatures is important and I am sorry that nothing has been done in that direction and hope that we can get some work done in that field this year. I am not certain, however, that his general criterion for allotropic changes would apply to an allotrope which must take place in a condition of high mechanical cohesion, such as steel is, at a temperature in the blue-heat range. There are certain facts available also, which might indicate that an allotrope need not always have to pass a certain equilibrium range before it begins to change into the other more stable allotrope. Also, it might be easily possible to have the two allotropes

mutually stable in various proportions throughout a considerable temperature range.

FRANCIS B. FOLEY, Bedford Hills, N. Y. (written discussion).—Since Doctor Jeffries' paper deals with the more unusual changes in iron and steel, as apart from the old and well-known changes, it would seem pertinent to the matter under discussion to call attention to the work of Felix Robin.[35] His method was to heat bars of steel to various temperatures, measuring the temperature with a thermocouple, and determine the duration of the sound resulting from tapping the bar while at these elevated temperatures. He plotted curves, duration of sound in seconds vs. temperature, and found, in commercial iron, a minimum at about 125° C. from which point the curve rose to a maximum between 220° and 250° C. and then dropped to almost zero at 540° C. After annealing, the curves had the same shape and the addition of carbon did not do away with the period of aphonia at 125° C. He always got a sharp drop from room temperature to the minimum at 125° C., then the marked rise to the maximum, followed by a gradual falling off in the duration of sound until a temperature of 450° C. was reached. There is a discussion by Osmond in which he suggests the possibility of a point low in the temperature scale. This curve of acoustic properties seems to follow closely that of the elastic limit referred to by Doctor Jeffries.

HOWARD SCOTT,* Washington, D. C. (written discussion).—It must be acknowledged, from a consideration of Doctor Jeffries' paper, that there is definite evidence indicating the probable existence of a low-temperature allotropic modification of iron that deserves intensive consideration. Doctor Jeffries quotes, however, some phenomena that cannot be accepted as evidence of low-temperature allotropy in iron.

One phenomenon is that of the transformation of cementite at about 200° C., the magnetic characteristics of which have been studied thoroughly by Honda and his co-workers. The evidence is conclusive that it is a phenomenon of free cementite only, so it can hardly explain the maximum at about 250° C. in the tensile-strength curve of Armco iron.

The low-temperature thermal change referred to as found in nickel-chromium steel is found also in other air-hardening steels on cooling and in carbon steels on very rapid cooling. It is commonly called Ar'' and is the A_{2-3} transformation that takes place when the resulting constituent is martensite. The identity of this transformation has been established by a number of observers and is discussed in a paper by the writer[36] where references to some of the researches are given. The

[35] F. Robin: Variations in the Acoustic Properties of Steel. *Carnegie Scholarship Memoirs*, Iron and Steel Inst. (1911) **3**, 125.

* Assistant Physicist, U. S. Bureau of Standards.

[36] *Trans.* (1920) **62**, 689.

temperature of this transformation (Ar'') is quite variable, depending on the composition of the steel and the amount of carbide in solution. This phenomenon likewise furnishes no argument for a low-temperature allotrope in iron.

In regard to the spontaneous generation of heat in recently hardened steel and the allied phenomenon of a heat evolution observed by means of heating curves, I may say that we have taken a rather elaborate series of curves on hardened carbon steels, the results of which will be ready for publication soon. A heat evolution starts at a relatively low temperature, gradually increases to a maximum, and ends abruptly at about 270° C. for a very slow heating rate. The thermal change is closely related to the change in other physical properties on tempering. The only logical interpretation I can give to this phenomenon is that it is the heat evolution of the cementite precipitations prevented by rapid cooling; it is clearly evident that this is the cause also of the heat evolution and contraction of recently hardened steels. It is not necessary, however, to presuppose a new allotropic modification of iron in this region to explain the phenomenon, for we find an analogous one in the case of duralumin;[87] but it is quite conceivable that the existence of such an allotrope would influence the characteristics of the cementite precipitation.

On the whole, the evidence is suggestive, but not conclusive as to the existence of a new low-temperature allotropic modification of iron. Proof of hysteresis in the tensile-strength curve inflection would do much to establish it as a manifestation of allotropy, as Doctor Hoyt suggested in the discussion of a previous paper by the author. A study of the effect of alloying elements on the position of the inflection would give invaluable information on the present problem and also as to the function of these elements in steel.

The phenomenon of "blue brittleness" can hardly be attributed to the hypothetical low-temperature allotrope of iron, for the former phenomenon is related to a much higher temperature than the latter. The most natural guess to make as to the cause of this pheomenon would be that it is due to a slight change in solubility of ferrite for cementite with temperature. This appears to be a logical hypothesis to work on for, as Doctor Jeffries shows, there is a time effect and the phenomenon is observable in annealed steels. Due to the finer state of division of the carbide, it might be supposed also that the effect would be greater in hardened than in annealed steels, which I believe is actually the case.

With the object of determining any small change in solubility of ferrite for cementite under the critical range, I have obtained some density values on an annealed eutectoid carbon steel and on Armco iron plate as received, followed by quenching in water from several temperatures

[87] *Trans.* (1920) **64**, 41.

at which the two samples (1 in. by 1½ in. by ⅜ in.) were held 1 hr. Since Doctor Jeffries has suggested that such work may be of value to the problem at hand, I present these preliminary results in the form of curves; see Fig. 1.

As anticipated, the changes are small and are negligible below 400° C., in which region they give no evidence of a structural change related to a critical point. Above 400° C., the decrease of density may be attributed to a slight increase of solubility of ferrite for cementite. This holds for the Armco iron as well as the eutectoid steel, as there are always fine

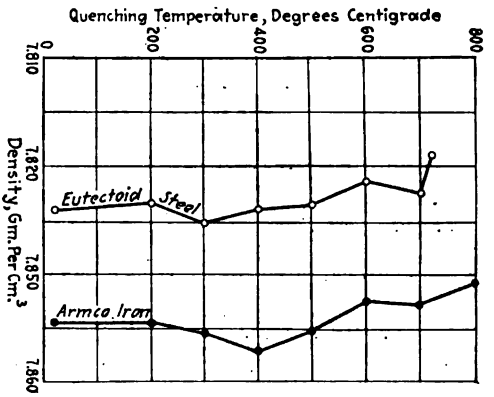


FIG. 1.

strings of cementite, although no pearlite is present in this iron, the carbon content being about 0.027 per cent. which might conceivably be responsible for the effect noted. These results do not prove the absence of a low-temperature allotrope, for it is not possible to prevent an allotropic change by rapid cooling alone. Quenching pure iron from above A_3 would not be expected to change its density appreciably.

In conclusion, I would like to ask Doctor Jeffries if he does not think that a slight stiffening of the ferrite matrix by the absorption of a small quantity of cementite would account for the higher impact values and change of path of rupture observed on quenching from certain temperatures under the critical range?

Effect of Time in Reheating Quenched Medium-carbon Steel below the Critical Range

By Carle R. Hayward,* Daniel M. MacNeil,† and Raymond L. Presbrey,†
Cambridge, Mass.

(New York Meeting, February, 1922)

At the February, 1916, meeting of the Institute, a paper presented by Hayward and Raymond gave the results of a study on the effect of time in tempering medium-carbon steel, when the following conclusions were reached:

It is not fair to consider the question settled when only three specimens were used for each treatment, but the results obtained indicate that for reheating quenched medium-carbon steel to temperatures below 500° it is only necessary to heat it through. Longer heating has little or no effect on the tensile strength, ductility, or hardness. At temperatures above 500°, increasing the time of treatment causes a slight falling off in hardness and tensile strength with a corresponding increase in ductility.

In the discussion of the paper these conclusions were attacked and evidence was presented that seemed to throw doubt on their accuracy. The authors, however, showed that this evidence was based on high-carbon or alloy steels and no facts regarding medium-carbon steel were presented.

During this study the heat treatment was carried out in a small electric resistance furnace. It held nine specimens, but when these were placed in the furnace the temperature was lowered to such an extent that 30 to 40 min. were required to reach the desired heat. The authors pointed to this as a weak point in the investigation and it seemed wise to supplement the research by work on similar steel but using a different method of heating. This has been done and the results are given in the present paper. The Rhode Island Tool Co. coöperated by furnishing the steel and turning the tensile specimens.

The steel used in this investigation came in three bars ¾ in. in diameter; analyses are as follows:

Bar Number	Carbon, Per Cent.	Manganese, Per Cent.	Phosphorus, Per Cent.	Sulfur, Per Cent.
1	0.46	0.56	0.010	0.055
2	0.44	0.58	0.007	0.042
3	0.48	0.58	0.007	0.048

*Associate Professor of Metallurgy, Massachusetts Institute of Technology.
†Senior student, Massachusetts Institute of Technology.

Heat Treatment

The specimens were quenched at 850° C. and then reheated in lots of three for 5, 15, 30 min., 1, 2, and 4 hr. at 300°, 400°, 500°, and 600° C. Three specimens cooled in the furnace, from 850° C., and three were tested in the quenched condition.

The bars were cut into 5½-in. (13.97 cm.) lengths and heated in a No. 1 oven furnace made by the American Gas Furnace Co. The furnace was heated to 900° C. and one third of the specimens introduced on an asbestos board that was supported 2 in. (5 cm.) above the bottom of the furnace. This lowered the temperature to about 800°, but after 20 min. it rose to 850°, at which point it was held for 10 min. Then the asbestos board was removed and the specimens quickly dumped into a tank of water. This operation was repeated until all but three of the specimens were quenched; these were allowed to cool in the furnace.

The quenched specimens were reheated, in lots of three, by immersing in a gas-heated pot containing about 75 lb. of type metal. The introduction of the specimens caused no appreciable change in the temperature of the metal and a constant temperature was easily maintained. The three specimens were fastened to an iron rod, to hold them below the surface of the metal and to facilitate their removal. After reheating for the desired time, the specimens were removed from the pot and quickly plunged into water.

Marking and Preparing the Specimens

Previous to quenching the specimens, a system of marking was devised to make identification easy. The first number indicates the temperature of reheating, 3 = 300°, 4 = 400°, 5 = 500°, 6 = 600°. The second number indicates the bar number, 1, 2, or 3. The third

Table 1.—*Markings of Specimens*

Specimen Number	Drawing		Specimen Number	Drawing		Specimen Number	Drawing	
	Time	Temperature, Degrees C.		Time	Temperature, Degrees C.		Time	Temperature, Degrees C.
10	Quenched		422	15 min.	400	536	4 hr.	500
20	Quenched		423	30 min.	400	621	5 min.	600
30	Quenched		424	1 hr.	400	622	15 min.	600
311	5 min.	300	425	2 hr.	400	623	30 min.	600
312	15 min.	300	426	4 hr.	400	634	1 hr.	600
313	30 min.	300	531	5 min.	500	635	2 hr.	600
314	1 hr.	300	532	15 min.	500	636	4 hr.	600
315	2 hr.	300	533	30 min.	500	1A	Annealed	
316	4 hr.	300	534	1 hr.	500	2A	Annealed	
421	5 min.	400	535	2 hr.	500	3A	Annealed	

number indicates the time of reheating, 1 = 5 min., 2 = 15 min., 3 = 30 min., 4 = 1 hr., 5 = 2 hr., 6 = 4 hr. A complete list of the markings is given in Table 1.

After the heat treatment, a ½-in. (12.7 mm.) piece was sawed from the end of each specimen for microscopic examination and hardness tests and the remaining 5-in. (12.7 cm.) lengths were turned into standard threaded tensile-test specimens with 2-in. gage length and 0.505-in. diameter.

Tensile and Hardness Tests

The machined and threaded specimens were first marked with the 2-in. gage mark and their diameters measured. They were then tested on a Tinius-Olsen autographic machine of 60,000 lb. (27,216 kg.) capacity

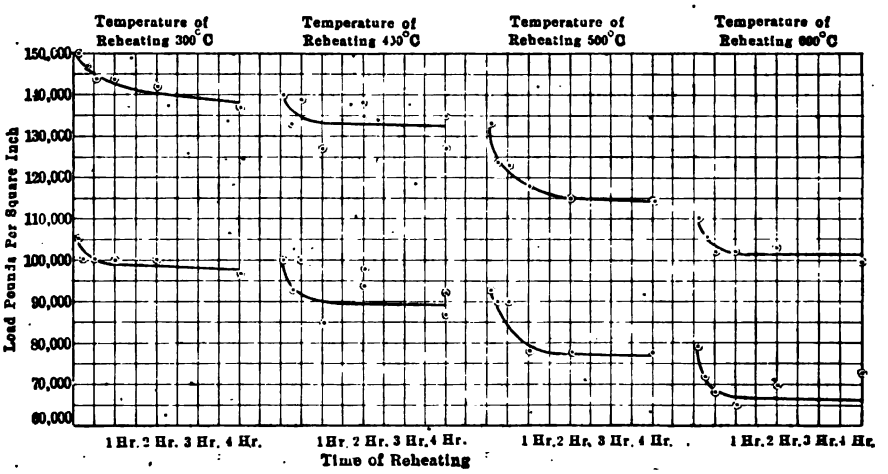


FIG. 1.—RESULTS OF TENSILE TESTS; UPPER CURVES SHOW BREAKING LOAD, LOWER CURVES SHOW YIELD POINT.

in the testing materials laboratory of the Massachusetts Institute of Technology. The autographic attachment was operated by the expansion of the specimen under the load and gave a plotted result of load elongation for the specimen.

From the curve, the yield point could be easily obtained, also the maximum and breaking loads. The use of the autographic attachment was especially valuable in the case of the high-carbon specimens as the determination of the yield point by the drop of the beam is liable to considerable error. Slow speed was used on the tests and when the specimens had been broken, they were measured for elongation and for decrease in diameter.

The average figures for yield point and maximum load are plotted in Figs. 1 and 2. It should be noted that, in several instances, a figure that obviously was faulty was not included in the average.

Microscopic examination of the pieces sawed from the ends of the specimens showed the usual structures. The photographs are not included in this paper. The pieces used for microscopic examination were used for hardness tests with an alpha Brinell machine and the Shore scleroscope. The results are given in Table 2.

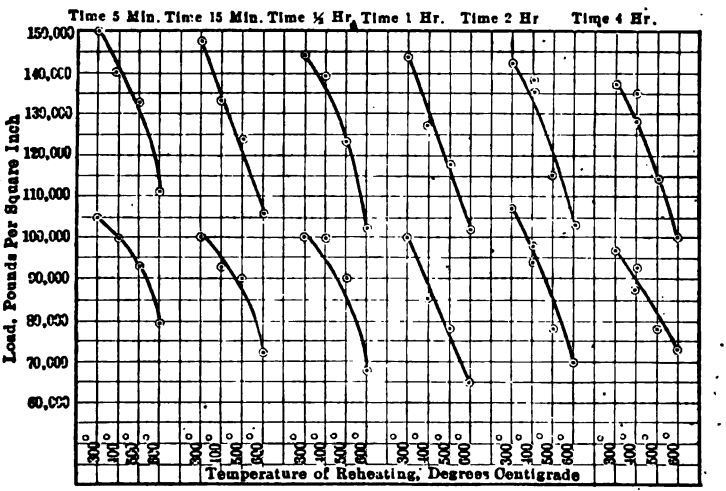


FIG. 2.—RESULTS OF TENSILE TESTS; UPPER CURVES SHOW BREAKING LOAD, LOWER CURVES SHOW YIELD POINT.

TABLE 2.—*Results of Hardness Tests*

Specimen Number	Brinell Hardness	Shore Hardness	Specimen Number	Brinell Hardness	Shore Hardness
10	285	42	531	297	26
20	302	43	532	277	18
30	321	45	533	251	21
311	280	24	534	269	17
312	302	27	535	243	22
313	302	20	536	245	23
314	285	17	621	225	18
315	306	25	622	214	21
316	272	28	623	217	25
421	293	33	634	222	24
422	285	22	635	217	20
423	290	23	636	209	21
424	272	17	1A	133	15
425	257	19	2A	126	16
426	272	21	3A	140	17

NOTE.—Shore hardness is the average of six readings.

Discussion of Results

In spite of the fact that great care was taken to secure uniform treatment of the three specimens in each set, some sets show erratic results. In four cases, the results were obviously low so the figures were rejected. In all other cases the average of the three results was plotted in the curves. The following points may be properly emphasized.

1. Even 5 min. heating of the quenched steel at 300° C. lowers considerably the strength and hardness and increases the ductility.

2. There is a marked increase in ductility in passing from the 400° to the 500° treatment without an equivalent lowering of strength; it is accompanied, however, by a change from an indefinite to a definite yield point. This was clear on the original load-elongation curves, which are not reproduced here. Although the annealed specimens from the three bars showed the same yield point and ultimate strength, there was a difference in the ductility; this explains drop in ductility between the ½ hr. and 1 hr. treatment at 600° when the bar changed from No. 2 to No. 3.

3. The specimens reheated to 600° C. are nearly as ductile as the annealed specimens, but they have an elastic limit about 60 per cent. greater.

4. In spite of several irregularities in the curves, it is evident that reheating the steel for 1 hr. is all that is necessary and there are indications that for temperatures of 400° and below, ½ hr. is sufficient. This confirms the work of Hayward and Raymond and also bears out the statement of Goerens[1] that "the influence of time becomes more decided as the temperature of annealing increases . . . It is clearly indicated that each particular temperature of annealing corresponds to a definite tenacity and elongation which is practically independent of the annealing period when once the duration of the annealing has lasted from a few minutes to about an hour according to the height of the temperature."

[1] Influence of Cold Working and Annealing on the Properties of Iron and Steel. Iron and Steel Inst., *Carnegie Schol. Mem.* (1911) **3**, 384.

Tensile Properties of Boiler Plate at Elevated Temperatures*

By H. J. French,† Met. Engr., Washington, D. C.

(New York Meeting, February, 1920)

At the request of a committee of the Engineering Division,[1] National Research Council, a study of the properties of boiler plate at various temperatures up to about 900° F. (482° C.) has been instigated. The following is a report of preliminary tests made on two grades of ½-in. plate and includes a description of the apparatus used in the determination of the proportional limit.

Detailed reference to the many published investigations in connection with the properties of steel at various temperatures will be omitted from this report. Suffice to state that results obtained for variation in tensile strength, elongation, and reduction in area with temperature are in substantial agreement with the effects now generally considered to be correct. Comparison of proportional limit values with results obtained by other investigators will be found in the conclusions.

Materials Used

The steels tested were ½-in. (12.7 mm.) open-hearth boiler plate of firebox and marine grades. The specified tensile strength and the analysis for each are shown in Table 1. In the manufacture of this material, a

Table 1

Series	Grade	Specified Tensile Strength, Lb. per Sq. In.	Ladle Analysis			
			Carbon, Per Cent.	Manganese, Per Cent.	Phosphorus, Per Cent.	Sulfur, Per Cent.
1	Firebox	52,000 to 62,000	0.19	0.43	0.020	0.031
2	Marine	60,000 to 70,000	0.25	0.38	0.019	0.031

* Published by permission of Director, U. S. Bureau of Standards.

† Chief, Heat Treatment Section, Division Metallurgy, U. S. Bureau of Standards.

[1] Committee on Physical Changes in Iron and Steel Below the Thermal Critical Range, Dr. Zay Jeffries, Chairman.

piping steel was avoided, the bath being kept in a boiling condition up to the moment of casting. In its cast condition, the metal is, therefore, porous and probably shows considerable segregation. While the tabulated ladle analyses probably represent the average composition of the steel, under such conditions of manufacture variations in individual plates are to be expected, depending on the portion of the ingot from which they were obtained.

A record of original ingot size, together with amount of reduction received during rolling, is shown in Table 2:

TABLE 2

Series	Grade	Original Wgt., Lb.	Ingot Size, Inches	Reduction in Rolling	Pattern Size, Inches
1	Firebox, 52,000 to 62,000 lb. tensile strength	5,900	36×15	30 to 1	36×18
2	Marine, 60,000 to 70,000 lb. tensile strength	3,650	32×12	24 to 1	36×12

FORM OF TEST BAR

Patterns 36 in. by 18 in. or 36 in. by 12 in., as shown in Table 2, were taken from the rolled plates, but unfortunately no record of their location with respect to the ingot is available. Flat test bars of the form and dimensions shown in Fig. 1 were cut from these patterns, the long dimension in each case being taken in the direction of rolling.

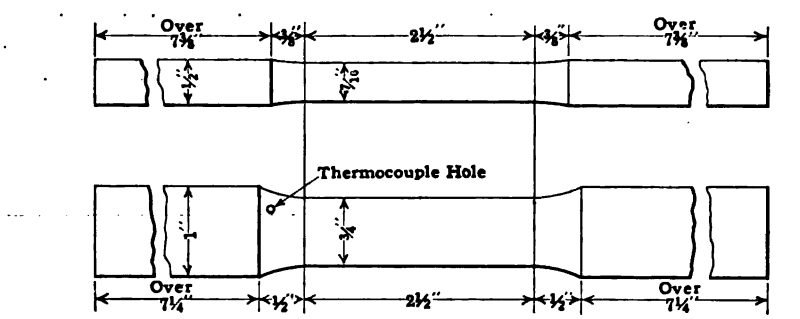


FIG. 1.—FLAT TEST BARS, LONG DIMENSION BEING TAKEN IN DIRECTION OF ROLLING.

APPARATUS FOR DETERMINATION OF PROPORTIONAL LIMIT

The apparatus used in the determination of the proportional limit at various temperatures is shown in Fig. 2. It consists primarily of two aluminum-alloy frames each rigidly fastened to a quenched and tempered

steel yoke (shown in Fig. 3) by two annealed, low-carbon steel rods. The specimen passes freely through the holes in the base of each of the frames.

The yokes are clamped to the specimen by three quenched and tempered high-speed steel screws. The tendency for the yoke to spread when considerable force is used in setting the screw is overcome by an additional bolt. The flanges on the upper frame are so arranged that two Ames dials may readily be securely fastened to them while those of the lower frame are capped with polished steel plates to give a smooth bearing surface to the pistons of the dials.

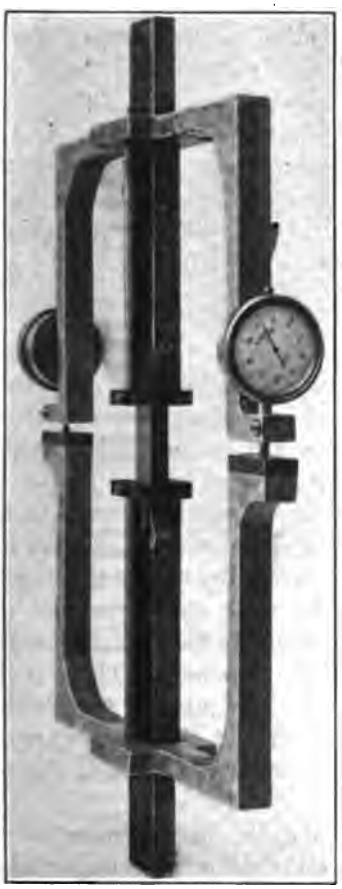
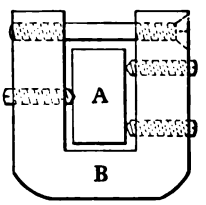


FIG. 2.—APPARATUS USED FOR DETERMINING PROPORTIONAL LIMIT.

The smallest division on the dial is equal to 0.001 in. (0.025 mm.) but estimated readings to the nearest 0.0001 in. (0.0025 mm.) may readily be taken. When stress is applied to the specimen, half the algebraic sum of the deformations recorded by the two dials represents the deformation of the specimen, which is centrally located with respect to the entire apparatus. For example, upon



A-Specimen
B-Yoke

FIG. 3.—CARBON-STEEL YOKES.

application of load, the apparatus may twist to some extent the dial on the left showing a negative deformation of 0.004 in. while that on the right registers a positive deformation of 0.009 in. Half the algebraic sum [½ (+ 0.009 in. − 0.004 in.) = 0.0025 in.] represents the deformation of the specimen under the load applied.

HEATING FURNACE

The test specimen was heated by means of an electric tube furnace of the form shown in Fig. 4. Two spiral resistors in series are used. The

one covers the entire length of the inner tube (11 in.) and the other is concentrated at the ends, the two requiring about 80 ft. (24 m.) of 22-gage chromel wire. The yokes and major part of the 18 in. (46 cm.) test bar and rods are contained in the heating chamber, which is 11 in. long. A comparatively small temperature gradient is obtained under suitable operating conditions as the effective heating length during determination of the proportional limit and tensile strength is about one-third of this at the center of the tube length, or approximately 3 in. The furnace is operated on either 110 or 220 volts, direct current, close regulation being obtained by two 15-ohm 30-ampere variable resistances in series in the circuit.

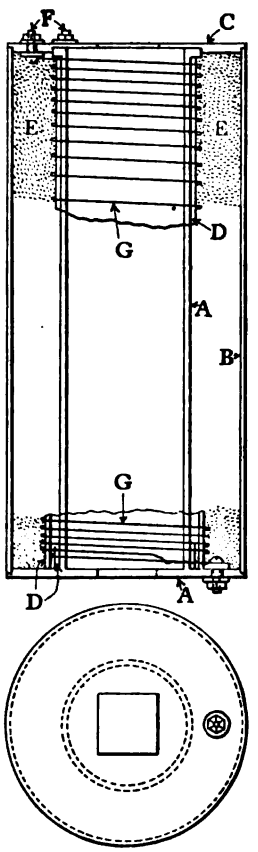


FIG. 4.—HEATING FURNACE.

A—INNER TUBE AND BASE (WELDED). B—OUTER TUBE. C—TOP PLATE. D—MICANITE AND ASBESTOS INSULATION. E—INFUSORIAL EARTH. F—TERMINALS. G—NICHROME RESISTORS.

TEST PROCEDURE

The method of setting up the apparatus, together with the procedure followed in actually carrying out the test, is substantially as follows: The specimen is marked on one surface with a double-pointed center punch leaving marks exactly 2 in. apart. The yokes are then attached to the specimen, the single screw being set into these impressions. Then, by lightly tapping the opposite side of the yoke containing the two screws, a light impression of their exact location can be obtained on the specimen. These points are then enlarged by the use of the double-pointed center punch and the yokes carrying rods and frames are firmly attached to the test piece.

The bolts holding the upper frame to the two rods are next taken off and the upper frame is removed. The specimen is then passed up through the furnace until the rods appear above the top and the upper frame is again fastened to the rods. The furnace is then placed on a stand and the specimen placed in the jaws of the testing machine, after which the dials are attached to the frame and adjusted to read zero. The completely assembled apparatus is shown in Fig. 5.

When the desired temperature and thermal equilibrium have been reached, a unit load approximating 1500 to 3000 lb. is applied, and the dials are again set at zero. Readings are then taken at increments of 500

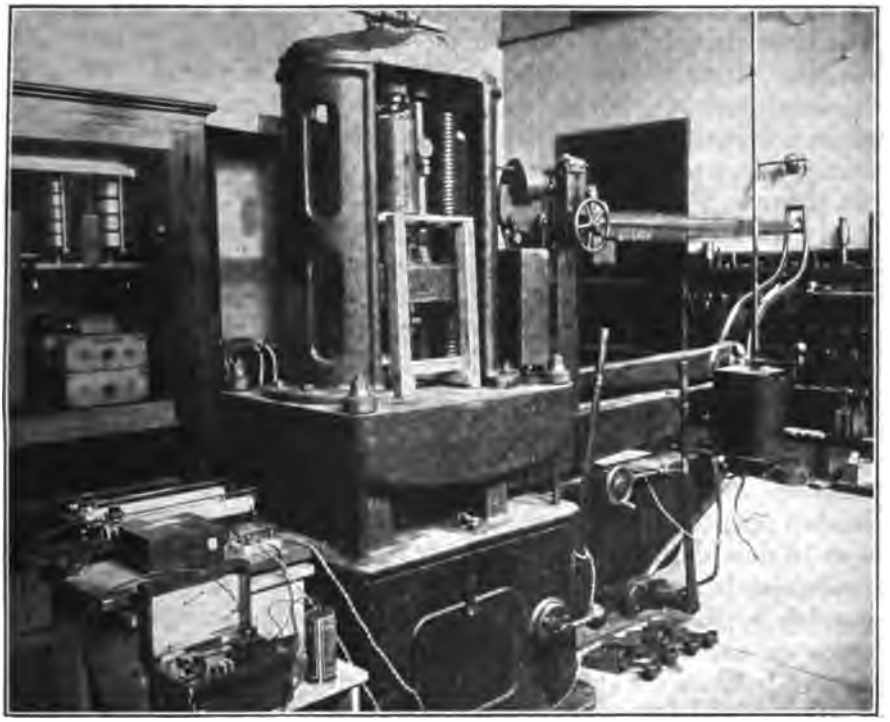


FIG. 5.—ASSEMBLED APPARATUS FOR DETERMINING PROPORTIONAL LIMIT.

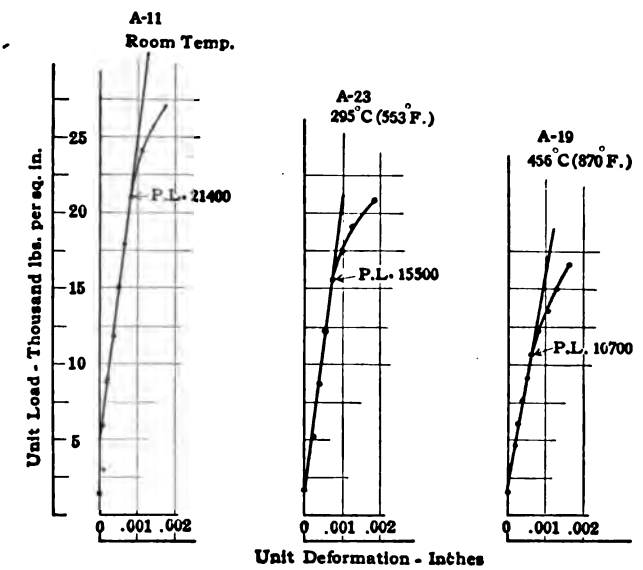


FIG 6.—STRESS-STRAIN DIAGRAMS OF BOILER PLATES AT VARIOUS TEMPERATURES.

or 1000 lb. (actual load) until the proportional limit has been passed. The dials are then removed and the specimen is broken in the usual manner. Tests at each temperature are made in triplicate. The proportional limit is obtained from a stress-strain diagram, in which unit stress is the ordinate and unit deformation the abscissa. Typical curves obtained from tests at various temperatures throughout the range covered are shown in Fig. 6.

Temperature is measured by a 22-gage standardized chromel-alumel couple connected to a Leeds & Northrup portable potentiometer. The end of the couple is inserted directly into a small hole drilled in the specimen at the fillet, its exact location being shown in Fig. 1.

Thermal Equilibrium

In order to obtain reliable and satisfactory results with the method described in the preceding paragraphs, thermal equilibrium must be reached prior to the start of the loading and maintained during the actual 8 to 15 min. during which the test is being carried out. The variable resistances in series in the electrical circuit make current adjustment possible so that the loss of heat from the heating unit, ends of test specimen and auxiliary apparatus by radiation, convection, and conduction balances the energy added to this entire system.

The effect of temperature variations may be large unless care is taken to allow sufficient time for the specimen to become uniformly heated throughout after the potentiometer has once indicated the desired temperature. The dial readings will assist in determining when equilibrum has been reached and is being maintained.

Emphasis is here laid on the fact that a suitable and readily manipulated apparatus for determining the proportional limit, and not the most accurate mechanism available, was sought. The material being tested is lacking in entire uniformity, so it appeared undesirable to erect an elaborate set-up requiring a great deal more time in actual test.

Temperature determinations under actual test conditions made by placing thermocouples in holes located at various points in a specimen carrying entire auxiliary apparatus, show that the position chosen for the single thermocouple in the fillet is representative of about the mean of the gradient throughout the gage length, where the temperature gradually decreases from top to bottom. This variation is within 54° F. (30° C.) and a maximum in the upper temperature ranges under consideration and does not exceed 36° F. (20° C.) at the lower temperatures used. However, as the thermocouple specimen with auxiliary apparatus and furnace are in the same relative position in each test, the results obtained at various temperatures throughout the range 70° to 870° F. (21° to 466° C.) are comparable.

Summary of Results Obtained

In Figs. 7 and 8 are shown the results of tensile tests obtained on firebox and marine grades of boiler plate at temperatures from 70° to

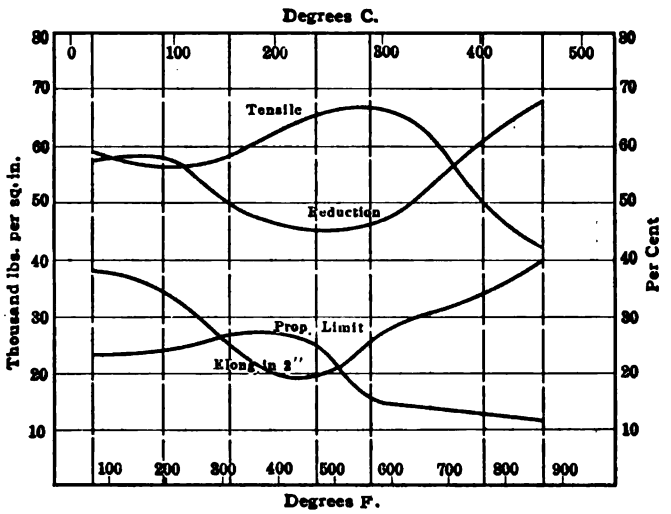


Fig. 7.—Tensile tests of ½-in. firebox grade boiler plate. Plates tested as rolled. C, 0.19; Mn, 0.43; P, 0.020; S, 0.031. Curves are average of three tests.

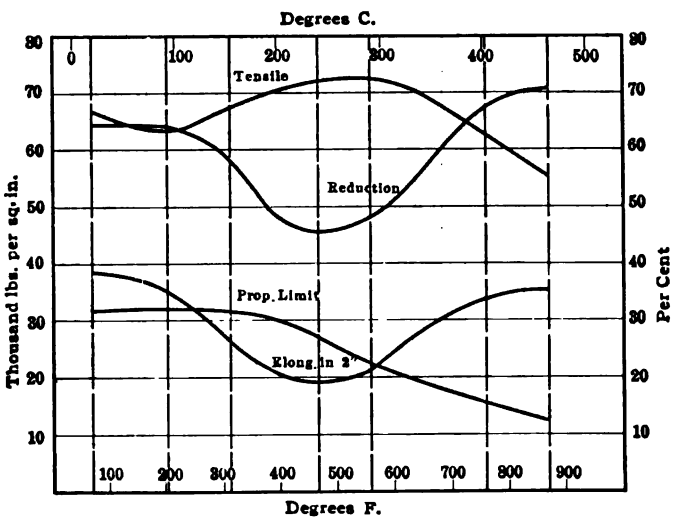


Fig. 8.—Tensile tests of ½-in. marine boiler plate. Plates tested as rolled. C, 0.25; Mn, 0.38; P, 0.019; S, 0.031. Curves are averages of three tests.

870° F. (21° to 466° C.). The curves are the average of three determinations at each of the pick-points, the temperatures chosen being repre-

TABLE 3.—*Tensile Tests of ½-in. Firebox Boiler Plate at Elevated Temperatures*

Sample	MV	Temperature		Proportional Limit, Lb. per Sq. In.	Maximum Strength, Lb. per Sq. In.	Per Cent. Elongation in 2 in.	Per Cent. Reduction of Area	Remarks
		Degrees C.	Degrees F.					
A11	Room temperature			21,400	59,500	29.0*	56.3	Broke in mark. Not in average.
A4				26,800	59,200	37.5	57.4	
A8				21,700	58,300	38.0	57.5	
Average.		21	70	23,300	59,000	37.75	57.1	
B10	3.9	91		23,500	57,650	34.75	57.6	Plates tested as rolled.
B20	3.9	91		23,700	54,450	34.75	57.3	
B13	3.9	91		23,700	54,500	34.5	59.2	
Average.		91	196	23,630	55,530	34.7	58.3	
B26	6.8	151		27,400	57,100	23.5	48.7	
B25	6.6	156		25,200	58,750	28.0	45.8	
B12	6.4	160		27,200	58,450	23.25	53.4	Carbon, 0.19 Manganese, 0.43 Phosphorus, 0.020 Sulfur, 0.031
Average.		156	313	26,600	58,100	24.9	49.3	
B7	10.2	243		25,400	65,000	18.75	41.8	
B23	10.1	240		25,700	64,600	21.0	46.8	
B21	10.2	243		23,600	65,800	19.75	46.6	
Average.		243	469	24,900	65,130	19.8	45.1	
A23	12.4	295		15,500	65,700	20.25	44.5	
A14	12.5	297		15,650	67,600	26.0	44.4	
A22	12.3	293		14,600	66,800	30.75	47.9	
Average.		295	563	15,250	66,700	25.7	45.6	
A18	17.4	412		13,300				
A17	17.3	410		11,800	47,700	*	60.6	
A15	17.2	407		13,750	50,600	33.5	60.3	
A21	17.1	402		13,000	49,150	34.0	61.3	
Average.		407	765	12,960	49,150	33.75	60.7	
A5	19.6	463		12,300	43,200	39.5	68.7	
A19	19.7	466		10,700	39,550	41.0	65.6	
A3	19.9	470		11,250	42,800	37.0	68.7	
Average.		466	871	11,430	41,850	39.2	67.7	

* Broke outside marks.

TABLE 4.—*Tensile Tests of ½-in. Marine Boiler Plate at Elevated Temperatures*

Sample	MV	Temperature		Proportional Limit, Lb. per Sq. In.	Maximum Strength, Lb. per Sq. In.	Per Cent. Elongation in 2 in.	Per Cent. Reduction of Area	Remarks
		Degrees C.	Degrees F.					
C1	Room temperature				66,500	38.0	64.3	Plates tested as rolled
D3				31,400	68,000	37.8	62.8	
C2				31,000	65,600	39.0	64.9	
Average.		21	70	31,200	66,700	38.3	64.0	
D10	3.9	91		32,000	64,800	36.25	65.2	
C12	4.1	91		31,000	62,000	34.75	63.3	
D12	4.1	96		32,300	62,700	34.75	63.3	Carbon, 0.25 Manganese, 0.38 Phosphorus, 0.019 Sulfur, 0.031
Average.		93	199	31,766	63,166	35.25	63.9	
C8	6.6	156		30,200	62,700	28.7	61.6	
D8	6.6	156		33,700	70,600	24.75	52.6	
C9	6.7	158		30,450	68,300	26.5	61.1	
Average.		156	313	31,450	67,200	26.65	58.4	
C6	10.2	243		26,200	69,900	20.7	46.5	
C7	10.2	243		28,000	72,300	18.7	48.4	
D7	10.0	238		27,500	72,700	19.5	41.7	
Average.		241	466	27,233	71,633	19.6	45.5	
C3	12.4	295		22,500	72,150	19.5	(40.6)	Bad break.
D5	12.3	293		23,750	72,350	22.0	51.5	
D11	12.3	293		21,100	73,000	22.0	45.0	
Average		293	559	22,450	72,500	21.25	48.2	Average 2 tests
D9	17.0	403		16,700	63,000	33.5	67.8	
C10	17.0	403		14,850	66,500	34.75	65.2	
C11	17.2	407		14,300	59,000	33.0	68.3	
Average.		404	759	15,933	62,833	33.75	67.1	
C13	19.6	463		12,600	55,100	35.0	68.8	
D13	19.6	463		12,400	55,100	34.0	72.4	
D14	19.9	470			56,500	36.75	71.0	
Average.		465	869	12,500	55,566	35.25	70.7	

sented by the vertical lines in these figures. Results forming the basis for these curves[2] are also given in Tables 3 and 4.

In both grades of plates increase in temperature from 70° to 870° F. (21° to 466° C.) is accompanied by distinct changes in strength and ductility, viz.: (*a*) The tensile strength at first decreases a few thousand pounds per square inch, reaching a minimum at about 200° F. (93° C.). This is followed by an increase up to about 550° F. (288° C.), where the tensile strength reaches a maximum about 10 per cent. greater than the normal room temperature value, after which another and final decrease occurs. (*b*) The percentage elongation in 2 in. (5 cm.) decreases rather slowly up to about 200° F. (93° C.) after which it drops more rapidly, until a minimum is reached at about 470° F. (243° C.). This factor then increases throughout the balance of the range under consideration. (*c*) The reduction in area closely follows the inflections registered in the curve for elongation but has a minimum at slightly higher temperature than the elongation. (*d*) The proportional limit at first increases slightly and shows a maximum in the neighborhood of 400° F. (204° C.) for the firebox plate and the highest values between 200 and 300° F. (93 and 149° C.) for the marine plate. It is noted that both the actual and the percentage increase are much greater in the case of the firebox grade and that the subsequent and final decrease in proportional limit for this plate takes place more sharply than in the case of the marine grade of boiler plate.

In the case of the firebox plate, the proportional limit is maintained above its original average room temperature value of 23,300 lb. per sq. in. to a higher temperature than is the case with the marine plate. It is probable that this may be associated with the greater mechanical work received by the firebox plate, as shown in Table 2.

The fact that the proportional limit "holds up" within a definite temperature range above normal before decrease occurs does not agree with data for mild steel published by Huntington[3] under the term elastic limit. However, Huntington's curve does not appear to be consistent with the actual results obtained and is based on rather too few tests. With the points actually given, a curve showing a similar effect to that obtained by the author might also justly be drawn. In this connection, it is interesting to note that a similar curve given by Huntington for

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[2] The values given for reduction of area were obtained from measurement of the minimum width and thickness of the fractured section and are not identical with values that would be obtained by the use of a planimeter, due to a decided necking in both this width and thickness in rectangular specimens.

[3] A. K. Huntington: The Effect of Temperatures Higher than Atmospheric on Tensile Tests of Copper and its Alloys and a Comparison with Wrought Iron and Steel. *Jnl.* Inst. Metals, (1912) **8**, 126.

wrought iron shows an increase with the first rise in temperature and a distinct maximum at about 300° F. (149° C.).

In their tensile tests on cold-rolled Bessemer steel shafting, Bregousky and Spring also have obtained a slight increase in yield point up to 300° F. (149° C.) with subsequent rapid decrease above this point.

In viewing the various factors as a whole, it is noted that the maximum tensile strength does not correspond to minimum elongation, minimum reduction in area or maximum proportional limit. This agrees with results obtained by Doctor Jeffries,[4] as clearly pointed out by S. L. Hoyt in discussion. Further work is now being carried on and a more complete report at a later date is contemplated.

Acknowledgment is made to Donald S. Clements, laboratory assistant, Bureau of Standards, for assistance rendered in development of the apparatus and in making the first series of tests, and to A. L. Meyer, chemical and metallurgical engineer, Lukens Steel Co., for his coöperation, and assistance rendered in the second series of tests.

DISCUSSION

HENRY D. HIBBARD, Plainfield, N. J.—This paper bears out the results obtained by Mr. Howard at the Watertown Arsenal, which were published in the Tests of Metals for the year 1888. He took as complete a series of steels as he could get, containing from 0.1 to 1 per cent. carbon, and found that all steels followed that same rule when tested at above atmospheric temperatures. He made quite an exhaustive study of the question, and published the results he obtained and curves for the various kinds of steel, showing the various properties.

I have found that report of great value. His work, done 30 years ago, is seldom referred to, and is almost unknown by engineers in general; but it was good reliable work, and from time to time some of the results that he obtained are corroborated, as in the present case.

THE CHAIRMAN (J. W. RICHARDS,* Bethlehem, Pa.).—It should perhaps be noted that the improvements in apparatus, particularly in electric heating furnaces, have made tests of this nature much more easy to reproduce now than those of 30 years ago so that they have facilitated greatly the task of any one doing similar work.

H. J. FRENCH.—What methods were used in determining the temperatures in Mr. Howard's work? In looking through the literature, I found thirty or forty references covering experiments at elevated temperatures but in the majority of cases the description of the methods

[4] Zay Jeffries: Effect of Temperature Deformation and Grain Size on the Mechanical Properties of Metals. *Trans.* (1919) **60**, 474.

* Professor of Metallurgy, Lehigh University.

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I believe so.

I would like to call attention to the fact that apparthe proportional limit and elongation follow each their variations than do the tensile strength and nsile strength seems to follow the reduction in area these curves.

used for determining the temperatures is rather vague or unsatisfactory. I am not familiar with Mr. Howard's article and would like to learn what method he used for heating his specimens and controlling the temperatures? That is one of the most difficult phases of the experimental work.

HENRY D. HIBBARD.—He used the Emery testing machine at Watertown, which is a horizontal machine; the pieces were heated with Bunsen burners underneath the machine. He determined the temperatures from the expansion of the test piece, using an extensometer reading to 0.0001 in., and considered that his temperatures were correct within 5° F.

H. J. FRENCH.—Were the pieces tested large or small?

HENRY D. HIBBARD.—The test pieces had diameters of 0.798 in. giving an area of cross-section of 0.50 sq. in. The gaged length was 5 inches.

CHAIRMAN RICHARDS.—I would like to confirm Mr. French's statement that the methods of heating were very inferior to the ones used at present, and the determining of temperatures was comparatively unreliable, as compared with our present methods. The data given in this paper are, therefore, in those two respects, far more reliable than those that possibly could have been given 30 years ago.

HENRY D. HIBBARD.—I think that is no doubt true. This question was first called to my attention in my first year in the steel industry. We were making boiler steel one day when one of the melters said, "Do you know how rotten this steel is?" I said, "No; what do you mean?" He heated a piece of boiler scrap that had been sheared off, bent it over on an anvil, and it broke; that is the same phenomenon that we have here. The fracture, when it was broken, was a bright, vivid blue, which fixes the temperature pretty well.

A. L. MEYER,* Coatesville, Pa.—The point of highest tensile strength here corresponds very closely to that pigeon-blue temperature range through which boiler makers fear to work their plates. The highest tensile strength and lowest ductility are shown at that temperature which, to the boiler maker, is a dangerous point and ignorance of this fact by the man working a plate through this temperature has been the cause of many "mysterious" failures in boiler plates.

CHAIRMAN RICHARDS.—In that connection, would it not be the maximum distance, or difference between the tensile strength and the proportional limit, that would determine the workability of the steel?

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* Chemist and Metallurgical Engineer, Lukens Iron & Steel Co.

A. L. MEYER.—I believe so.

H. J. FRENCH.—I would like to call attention to the fact that apparently we show that the proportional limit and elongation follow each other more closely in their variations than do the tensile strength and elongation, and the tensile strength seems to follow the reduction in area more closely in both these curves.

Critical Ranges of Some Commercial Nickel Steels

By Howard Scott,* Washington, D. C.

(New York Meeting, February, 1920)

The great advances made in mechanical engineering during recent years through the use of alloy steels, as illustrated by the development of the airplane and automobile, may be ascribed primarily to the application of nickel as an alloying element. The ternary system iron-carbon-nickel has a wide industrial application and forms, further, the fundamental basis of the even greater class of the widely used quarternary steels such as nickel-chromium, nickel-silicon, and nickel-vanadium. As is not uncommon with such cases of virile growth in an industry, the application of the alloy steel in a largely empirical manner has outstripped its scientific development so that a fertile field for metallographic research still remains. In this field, the basic nickel steels require first consideration and are the subject of the present investigation, which is offered as a preliminary to the study of the more complex alloys of industrial importance.

Of the principal tools of metallography—microscopic examination, determination of mechanical properties, and thermal analysis—the last has developed much more slowly in its application to industrial needs so that the situation often exists that heat treatment operations are based on empirically determined temperatures; that is, temperatures determined without regard to the actual transformation characteristics of the alloy. This situation is undesirable as there is no uniform standard for comparison of results. It is due, outside the usual difficulties involved in temperature measurements, to the pioneer character of much of the published work; to the lack of definiteness of the Ac_3 transformation,[1] particularly in low-carbon steels; to the failure to define operating conditions completely; and to the paucity of information correlating thermal characteristics with results of heat treatment.

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* Assistant Physicist, U. S. Bureau of Standards.

[1] Ac_3 and Ar_3 are used in the text to indicate this transformation whether above or below the maximum of A_3.

In pursuing the present investigation, the foregoing difficulties were recognized and precautions taken, where possible, to eliminate them with the object of collecting transformation-temperature data for the several compositions of nickel steels available at the Bureau of Standards as a basis to aid in the standardization and specification of thermal treatments for the nickel steels. A review is also included of the previous work in this field and attention is called to such phenomena as are related to the constitution of these steels.

Previous Observations on the Critical Temperatures of Iron-carbon-nickel Alloys

The previous investigators in this field have presented critical-temperature data on nickel steels obtained by the use of thermal analysis and also by employing the change in several of the physical properties as a criterion of allotropic change. The former method has been confined chiefly to steels having an appreciable A_1 transformation and the latter to iron-nickel alloys.

The attention of most experimenters seems to have centered on the iron-nickel alloys due, no doubt, to their peculiar properties and theoretical significance. There is, therefore, considerable material available in this field. The principal investigations have been those of Hopkinson, Osmond, Dumas, Guertler and Tammann and Honda and Takagi,[2] in which the changes in the magnetic state were used as a criterion of phase change. Boudouard[3] has used thermoelectric power, and Chevenard[4] expansion in the same way.

The results of Honda and Takagi being the most recent and apparently the most consistent, have been plotted in Fig. 1. Unfortunately they have not given the actual analyses of the material used so their results have not the weight that such careful experimental work deserves. The curve for Ar_3 indicates that Ar_3 occurs at absolute zero for a nickel content between 32 and 33 per cent. while the work of Chevenard[5] indicates that this transformation would be entirely complete at absolute zero for a nickel content between 34 and 35 per cent. This is good agreement, considering that different experimental methods have been used, and the interesting conclusion seems justifiable that above 34 per

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[2] Hopkinson: *Proc.* Royal Soc. London (1890) **48**, 1.
Osmond: *Compt. Rend.* (1899) **128**, 304.
Dumas: Fig. 89, p. 271 of Guillet's text "Etude Industrielle des Alliages Métalliques."
Guertler and Tammann: *Zeit. Anorg. Chem.* (1905) **45**, 205.
Honda and Takagi: *Sci. Rep.* Tohoku Imperial Univ. (1917) **6**, 321.

[3] Boudouard: *Jnl.* Iron and Steel Inst. (1903) **63**, 299.

[4] Chevenard: *Rev. de Met.* (1914) **11**, 841.

[5] *Op. cit.*

cent. nickel the iron at all temperatures is in the gamma state. This critical composition corresponds remarkably closely to that of Fe_2Ni (34.45 per cent. nickel).

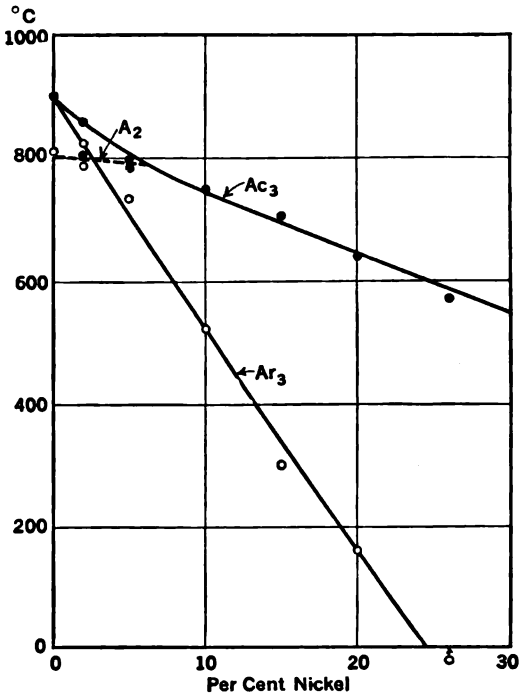

FIG 1.—TRANSFORMATION TEMPERATURES OF IRON-NICKEL ALLOYS MAGNETICALLY DETERMINED BY HONDA AND TAKAGI.

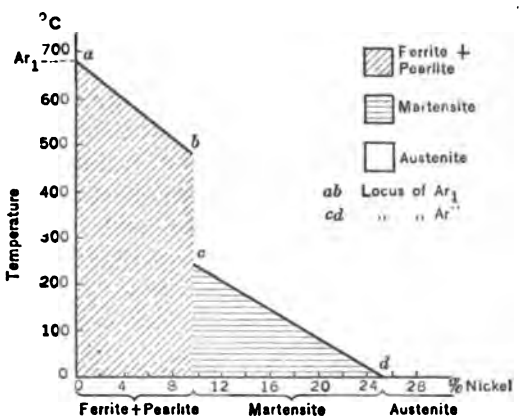

FIG. 2.—EFFECT OF NICKEL ON THE *Ar* CRITICAL RANGES OF 0.20 PER CENT. CARBON STEELS. (*Dejean.*)

In medium carbon-nickel steels two researches of considerable value are available, namely, those of Dejean and of Carpenter, Hadfield and

Longmuir.[6] The value of the contribution by the former author lies in the interpretations given to the thermal critical temperatures obtained from 0.20 per cent. carbon steels of various nickel contents and that of the latter authors in the more complete information given on variable nickel steels of 0.40 to 0.50 per cent. carbon content.

The cooling-curve data of Dejean, as plotted by him, are reproduced in Fig. 2, with changes only in the notation of his points of A to Ar_1 and B to Ar'', in accordance with that adopted by Portevin,[7] Chevenard and the author for describing the same phenomena as found in widely different steels. After showing that the transformation Ar_1 of this figure represents the precipitation of cementite as troostite or a decomposition product, he says (p. 671):

> There now remains to be determined the exact nature of the transformation occurring at point B (Ar''). The most universal opinion is that martensite is a metastable solid solution of cementite and ferrite or alpha iron. The point B (Ar''), thus from the foregoing, corresponds to the transformation of gamma iron into alpha without the carbide, which was in the gamma iron, being thrown out of solution. Fundamentally the point B (Ar'') is the Ar_3 point depressed.

Dejean[8] further illustrates these constitutional changes diagrammatically, as reproduced in Fig. 3 with the same notational changes as Fig. 2.

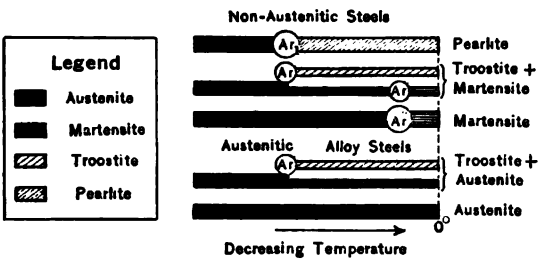

FIG. 3.—DIAGRAM OF CONSTITUTIONAL CHANGES IN COOLING STEELS. (*Dejean.*)

The same phenomenon is well verified by the investigations of Carpenter, Hadfield, and Longmuir already mentioned, although they offered no explanation of it. The transformation temperature data from their tables have been plotted in Fig. 4, together with their observations on the

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[6] Dejean: *Rev. de Met.* (1917) **14**, 641.
Carpenter, Hadfield and Longmuir: 7th Report to Alloys Research Committee, *Proc.* Inst. Mech. Eng. (1905) Pt. 4, 857.

[7] Portevin: *Rev. de Met.* (1917) **14**, 707; also Preprint Iron and Steel Inst., Sept., 1919.
Chevenard: *Ibid.*, 610.
Scott: *Trans.* (1920), **62**, 689. Also U. S. Bureau of Standards *Sci. Paper* 335.

[8] Dejean: *Compt. Rend.* (1917) **165**, 429.

microstructure of the same steels air-cooled from above Ac_2. A few corrections have been made to their values from the curves so that the tabulated results would be comparable on the basis of observations taken from derived differential or inverse-rate curves. Unfortunately, the temperature of the Ac_1 transformation cannot be estimated with any degree of certainty from the curves given.

In Fig. 4, the limits over which both martensite and troostite are found in the air-cooled samples have been indicated by dotted lines. Since Carpenter, Hadfield, and Longmuir did not examine microscopically their samples used for thermal study, it is impossible to set accurately

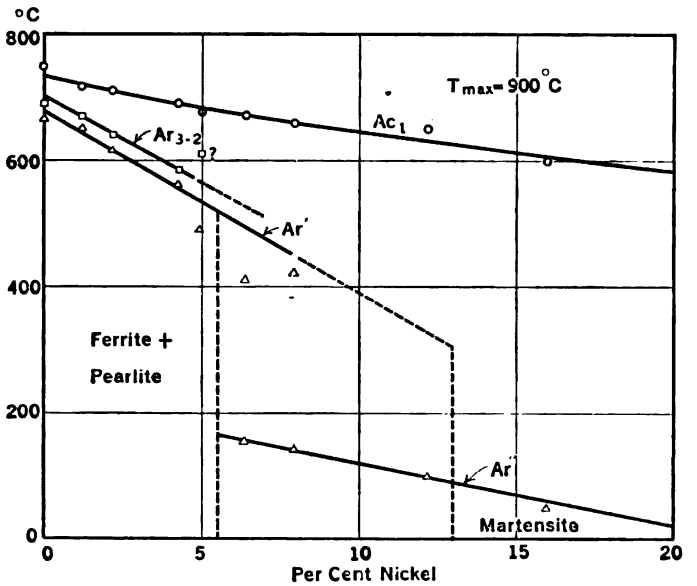

FIG. 4.—EFFECT OF NICKEL ON THE THERMAL CRITICAL RANGES OF 0.40 TO 0.50 PER CENT. CARBON STEELS FROM DATA OF CARPENTER, HADFIELD, AND LONGMUIR.

the limits of the range of nickel content over which, for the rate of cooling adopted, both martensite and troostite will be found and also the composition at which ferrite no longer separates out, but this latter is probably somewhere within the former region. The sharp temperature difference between Ar' and Ar_1 occurring between 4.5 and 9 per cent. nickel contents the author believes to be quite significant and to correspond to the formation of appreciable amounts of troostite, for the marked structural difference between troostite and pearlite would indicate a similar thermal difference.

Besides these investigations of the changes in the physical properties of nickel steels, Meyer[9] has studied microscopically the effect of nickel

[9] Meyer: *Stahlu. Eisen* (1914) **34**, 1395, 1456.

and manganese on the ferrite precipitation for various steels. He observed the appearance of ferrite on quenching steels heated above Ac_3 and then cooled to the quenching temperature. His results, which are for Ar_3, are of course not directly applicable to determining heat-treatment temperatures and have a further disadvantage of not agreeing well among themselves. Thus two steels not differing in carbon, nickel and silicon by more than 0.02 per cent. and in manganese by 0.13 per cent. give a 30° C. difference in Ar_3. His generalizations are also based on a curve for Ar_3 convex upwards, which is, of course, incorrect.

From the foregoing summary of previous investigations, it is apparent that considerable work has been carried out on a wide range of compositions, and that the A_1 transformation only has been definitely defined. The present work covers only a limited range of compositions, which are, however, of great industrial importance. The aim of this study is to define more completely and precisely the transformation ranges of these low-nickel medium-carbon steels.

Experimental Results

The work was carried out on seven commercial steels of a nickel content from 0 to 3.5 per cent., the proportion of other elements being fairly constant, and on a synthetic iron-carbon alloy made up at the Bureau of Standards.[10] The chemical compositions are given in Table 1. The thermal curves of these steels were obtained on samples of 1.5 to 2.0 gm. mass. The apparatus employed and the details of manipulation have been described somewhat in detail elsewhere.[11] Several runs

Table 1.—*Compositions of Steels Investigated*

Sample No.	Composition, Per Cent.						Remarks
	Carbon	Nickel	Manganese	Silicon	Phosphorus	Sulfur	
F30	0.40			0.008			Iron-carbon alloy, impurities probably less than 0.04 per cent.
C24	0.40	0.00	0.75	0.22	0.014	0.022	Nickel steels.
A50	0.38	2.00	0.66	0.16	0.017	0.011	
A49	0.35	2.04	0.65	0.17	0.010	0.020	
A58	0.35	2.68	0.64	0.24	0.014	0.022	
A51	0.40	2.90	0.63	0.28	0.023	0.033	
A52	0.37	3.00	0.71	0.22	0.012	0.010	
A53	0.29	3.46	0.56	0.28	0.018	0.028	

[10] Cain, Schramm and Cleaves: U. S. Bureau of Standards *Sci. Paper* 266.

[11] Scott and Freeman: U. S. Bureau of Standards *Sci. Paper* 348 and "Pyrometry," 214. A. I. M. E., 1920.

TABLE 2.—*Transformation Range Data of Steels Investigated—Temperature in Degrees C.*

Sample No.	Composition		Heating	Rate of Heating, Deg. C. per Sec.	Ac_1			Ac_2 Maximum	Ac_3		Temperature, Maximum	Rate of Cooling, Deg. C. per Sec.	Ar_2		Ar_1		
	Carbon, Per Cent.	Nickel, Per Cent.			Beginning	Maximum	End		Maximum	End			Beginning	Maximum	Beginning	Maximum	End
F30	0.40		First	0.09	732	735	746	767	781	799	880	0.10	772	759	709	705	699
			Second	0.21	734	737	746	766	794	817	885	0.21	772	753	707	703	692
			Third	0.16	732	736	746	768	789	810	885	0.17	758	724	708	704	691
Average..	.....	.....	.....	0.15	733	736	746	767	788	809		0.16	767	745	708	704	694
C24	0.40	0.00	First	0.19	729	733	764		787	808	855	0.19	741	726	(685)	(678)	(654)
			Second	0.15	725	731	746	760	785	803	850	0.15	741	732	678	670	649
			Third	0.10	723	729	744	758	779	798	845	0.10		737	676	670	660
			Fourth	0.30	727	733	747	759		805	850	0.16	742	729		667	654
C24′	0.40	0.00	First	0.15	728	733	753	762	784	800	885	0.16	737	723	(684)	(676)	(652)
			Second	0.13	725	738	746	760	783	802	885	0.13	741	727	678	671	650
			Third	0.075	722	728	741	757	777	794	870	0.080	748	733	678	670	655
			Fourth	0.17	726	733	746	760	783	807	885	0.16	748	725	687	676	661
Average..	.....	.....	.....	0.16	726	732	748	759	783	802		0.14	743	729	681	672	654
A50	0.38	2.00	First	0.23	697	712	724		741	762	845	0.23	693	668	639	629	596
			Second	0.11		709	722		735	757	835	Power off					
			Third	0.10	696	709	722		737	756	845	0.10	689	671	645	631	602
Average..	.....	.....	.....	0.15	696	710	723		738	758		0.16	691	670	642	630	599
A49	0.35	2.04	First	0.19	700	710	725		745	758	835	0.19	693	674	644	633	603
			Second	0.14	700	709	721		742	758	835	0.15	701	676	642	633	604
			Third	0.044	697	707	717		740		845	0.035		683	646	636	617
Average..	.....	.....	.....	0.12	699	709	721		742	758		0.13	697	678	644	634	608
A58	0.35	2.68	First	0.22	697	705	718		739	756	850	0.21	675	652	624	614	573
			Second	0.14	689	704	715		735	756	850	0.14	674	654	622	610	574
			Third	0.10	689	703	714		735	754	845	0.10	671	661	622	614	584
			Fourth	0.30	690	703	716		739	765	855	0.25	667	648	615	606	573
Average..	.....	.....	.....	0.19	691	704	716		737	758		0.18	672	654	621	611	576

A51	0.40	2.90	First	0.20	686	701	712		728	744	850	0.22	665	643	614	606	571
			Second	0.16	687	701	715		723	742	850	0.16	674	644	620	606	572
Average..	....	......	....	0.18	686	701	714		726	743		0.19	670	644	617	606	572
A52	0.37	3.00	First	0.26	694	705	717		732	753	845	0.25	665	638	620	608	562
			Second	0.11	677	701	717		726	748	845	0.11	672	644	613	610	572
Average..	....	......	....	0.19	688	703	717		729	750		0.18	668	641	616	609	567
A53	0.29	3.46	First	0.16	688	703			736	752	840	0.18	668	647	609	595	569
			Second	0.076	682	700	714		731	753	835	0.085	686	648	610	597	575
			Third	0.052	682	693	706		722	745	835	0.056		650		600	585
Average..	....	......	....	0.096	684	695	710		730	750		0.074	677	648	610	598	576

were taken on each composition and a curve typical of each is reproduced in Figs. 5 and 6 to illustrate the interpretation of the various thermal inflections. The temperature values taken from all the curves, as illustrated, are given in Table 2, together with such other data as are essential to the precise definition of the critical points. When, however, the transformation A_1 showed a decalescence or recalescence, which was only in the case of the steels not containing nickel, the temperature of the beginning of the reversal was then taken as the maximum. The intensity of this phenomenon, as observed in the carbon steels, is given in Table 3.

The difficulty, already mentioned, of locating Ac_3 is apparent from an inspection of Figs. 5 and 6. This is due to its position, *i.e.*, a superimposing on the end of Ac_1, and to its attenuated character. It may, however, be brought out with maximum sharpness by a suitable choice of heating rate; a decrease of rate causes a more pronounced inflection as illustrated by the second and fourth heatings of A58, Fig. 5. There is, however, a practicable limit to the benefit derived due to the increased variability of the time readings with increasing time interval. This limit is reached for the apparatus employed at a rate of about 0.05° C. per second, for which rate the individual readings are likely to be too variable to show the Ac_3 inflection clearly.

From the foregoing, the values of the Ac_3 transformation temperatures might be expected to be somewhat inconsistent, but this is not the case for there is very good agreement between the various curves as shown by Fig. 7 and Table 2. As a matter of fact, the more definite Ar transformations are less consistent than the Ac. This should not be ascribed to an inexplic-

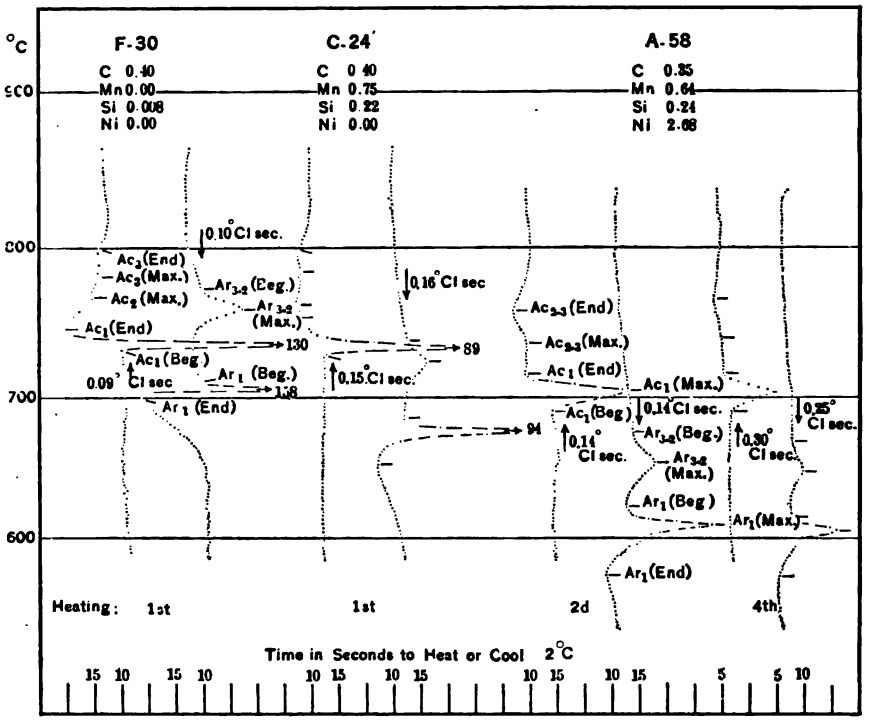

FIG. 5.—THERMAL CURVES OF CARBON AND NICKEL STEELS.

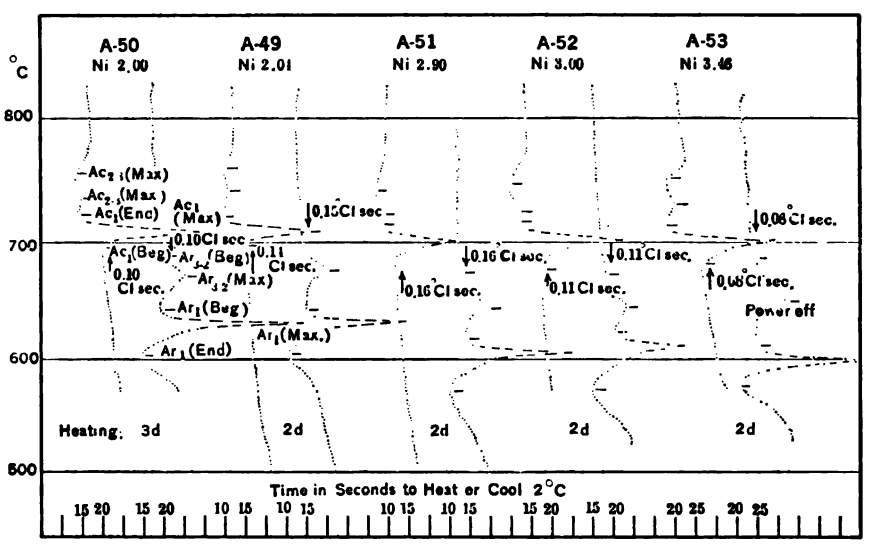

FIG. 6.—THERMAL CURVES OF NICKEL STEELS.

able variability of critical points, as is not unusual, but to actual constitutional differences in the metal due, no doubt, largely to previous

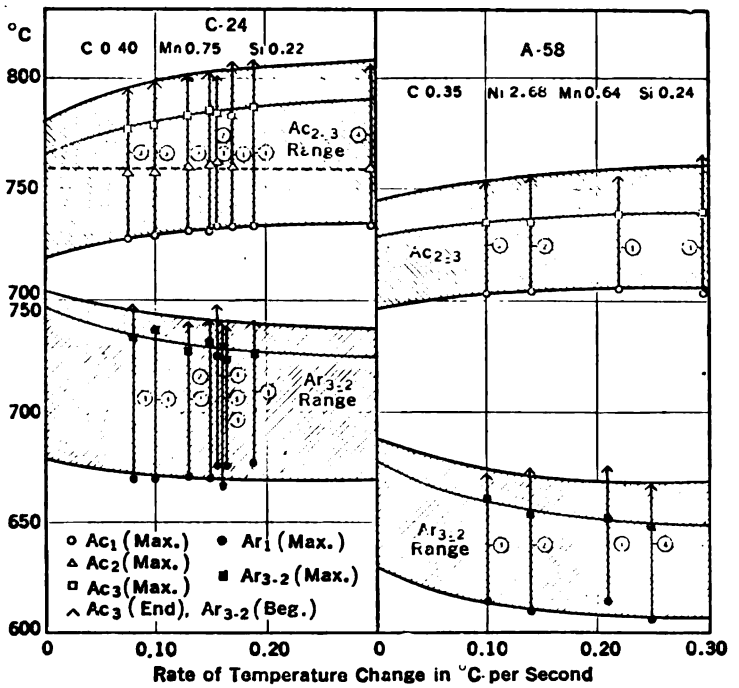

FIG. 7.—EFFECT OF RATE OF TEMPERATURE CHANGE ON THE CRITICAL RANGES OF A CARBON AND NICKEL STEEL.

TABLE 3.—*Intensities of Decalescence and Recalescence Effects Observed*

Sample No.	Heating	Rate of Heating, Degrees C. per Second	Decalescence, Degrees C.	Rate of Cooling, Degrees C. per Second	Recalescence, Degrees C.
F30	First	0.09	None observed	0.10	4.3
F30	Second	0.21	1.8	0.21	3.7
F30	Third	0.16	1.9	0.17	1.8
C24	First	0.19	None observed	0.91	0.3
C24	Second	0.15	None observed	0.15	0.2
C24	Third	0.10	None observed	0.10	0.8
C24	Fourth	0.30	None observed	0.16	0.5
C24′	First	0.15	None observed	0.16	None observed
C24′	Second	0.13	None observed	0.13	1.0
C24′	Third	0.075	None observed	0.08	0.4
C24′	Fourth	0.17	None observed	0.16	1.0

heat treatment. Thus, the first cooling of C24 and C24′, duplicate samples, shows Ar_1 6° and 4° C., respectively, above the average. Microscopic examinations of the steel in the initial state and after taking the thermal

curves showed that the structure in the former condition was quite coarse, while in the latter it was very fine. The behavior of Ar_3, for the iron-carbon alloy, in this connection, is also peculiar, the maximum being distinctly lower after each successive heating. As yet a satisfactory explanation of this cannot be offered. That the Ar_1 transformation should be more susceptible to previous thermal treatment than the Ac_1 is not sur-

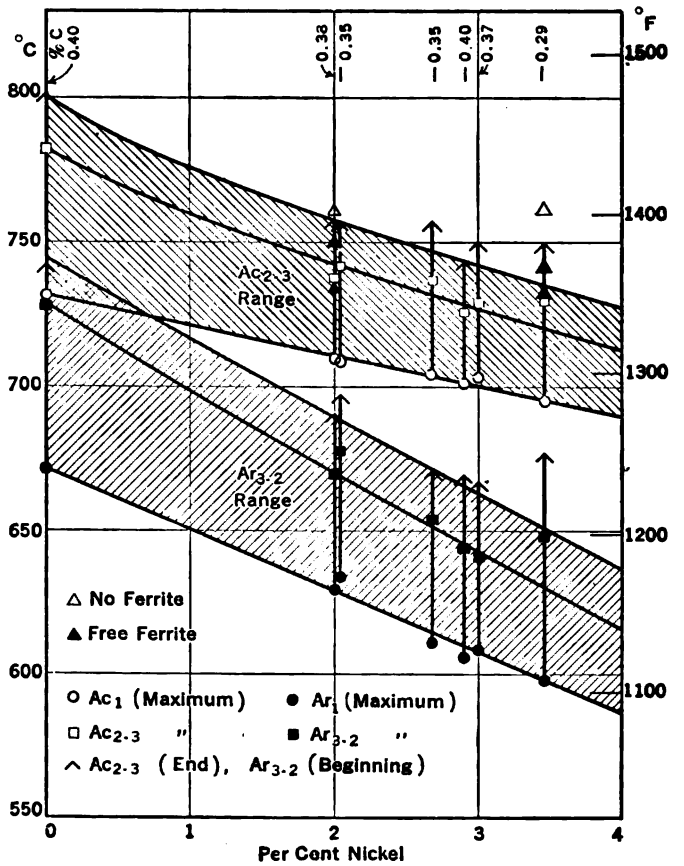

FIG. 8.—EFFECT OF NICKEL ON THE CRITICAL RANGES OF 0.40 PER CENT. CARBON STEEL.

prising in view of the greater effect of other variables—as rate of temperature change and composition—on its position, as shown in the following sections.

The principal data of Table 2 on two of the steels have been collected in Fig. 7 to illustrate the effect of rate of temperature change. From these curves, it is apparent that the critical ranges Ac are much less affected than Ar, but in both cases they vary approximately linearly over the range of rates employed. The effect of rate is slight so the values for each composition as given in Table 2 are averaged.

These mean values, for the points given in Fig. 7, have been plotted against per cent. nickel in Fig. 8, the values for zero nickel are those taken from the carbon steel C24. The curves are drawn to approximate conditions for 0.40 per cent. carbon steel and an average rate of temperature change of 0.15° C. per second. The structure of small specimens quenched in water after a 10-minute exposure at the temperature indicated was determined by microscopic examination. These results are indicated in Fig. 8 as triangles, of which the outlined ones represent a purely martensitic structure and the solid ones martensitic matrix containing free ferrite.

From these and other curves presented, the much greater effect of nickel on the *Ar* than on the *Ac* transformations is evident, but the effect of the other elements entering into the composition of steel in appreciable quantities is also quite marked. This is shown by a comparison of the results for the synthetic iron-carbon alloy F30 with the commercial carbon steel C24, which has the same carbon content, with silicon and manganese in addition, in approximately the same proportions as the nickel steels. The combined effect of these two elements, if the action of phosphorus and sulfur is considered inappreciable, is to lower the Ac_1 and Ac_3 ranges, as shown in Table 3, 4° to 5° C. and Ac_2 8° C., while they lower the Ar_1 transformation about 32° C. The lowering of A_1 and A_3 is due to the manganese, but its full effect is neutralized by silicon, which has the tendency to raise these critical ranges. It may be, however, that both elements contribute to the lowering of Ac_2.

Interpretation and Application of Experimental Data

The methods of obtaining the temperatures given for the Ac_3 transformation in hypoeutectoid steels are usually not completely specified but, in general, the temperatures chosen are those corresponding to the maximum of the thermal change of the inverse rate or derived differential heating curves. From the quenching experiments previously noted, and recorded in Fig. 8, it is evident that this point does not represent a temperature of homogeneous austenite solution, which exists only above a temperature 20° C. higher. This temperature corresponds closely with the point on the inverse-rate heating curves, here called the end of Ac_3. This, then, is a fundamental temperature of heat-treatment practice readily determinable by the two most widely recognized methods of metallography, and which should, therefore, be the temperature sought in critical-range determinations for the uniformity and standardization of metallographic practice and of thermal-treatment specifications.

The curves of Fig. 8 then furnish the fundamental data for determining the heat treatment of 0.40 per cent. carbon, 0 to 4 per cent. nickel steels and for correcting such thermal observations as indicate only Ac_3 maxi-

mum, but they do not furnish any guide to the treatment of steels differing much in composition from 0.40 per cent. carbon. Since carbon has a much more pronounced effect on the A_3 ranges than nickel, it may be of some value to outline a method of extrapolation to higher or lower carbon contents with a satisfactory degree of accuracy.

Since any means of extrapolation may be expected to depend on the relation between the A_3 transformation and the carbon content of simple steels, the curves representing the critical ranges on heating pure iron-carbon alloys have been reproduced in Fig. 9. These are taken from un-

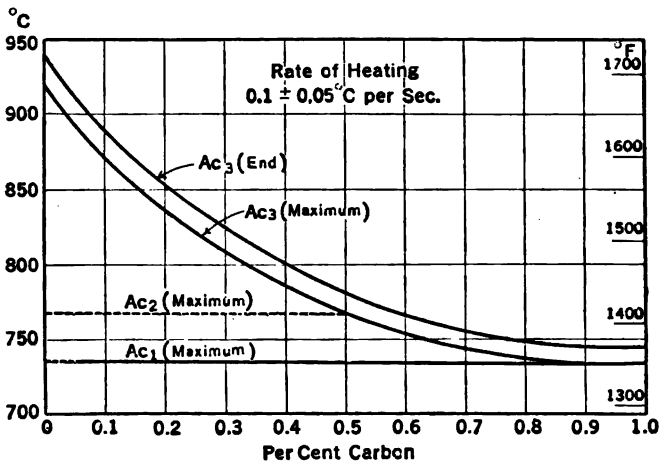

FIG. 9.—EFFECT OF CARBON ON *Ac* CRITICAL RANGES OF CARBON STEELS.

published data available at the Bureau of Standards and interpreted on the same basis as the curves presented here. The line representing the end of Ac_3 agrees within 10° C. with the observations of Howe and Levy[12] on the microstructure of quenched specimens of low-manganese steels, so from the preceding conclusions as to the effect of ordinary quantities of manganese and silicon on the *Ac* ranges, its accuracy is established for carbon steels well within the limits required in commercial work.

From this curve, the effect of various carbon contents for a given nickel content may be readily estimated on the assumption that the curve does not lose its characteristic form for that nickel content. This assumption appears justifiable as nickel (or a nickel compound) forms a solid solution with iron and does not affect the constitution of the carbide. To make, therefore, the proposed extrapolations, it is necessary only to correct for the familiar effect of nickel in lowering the critical ranges and the accompanying effect of nickel in shifting the eutectoid ratio.

[12] Howe and Levy: *Trans.* (1913) **47**, 587.

A consideration of the iron-carbon diagram, Fig. 10, leads one to expect the latter effect, a displacement of the eutectoid ratio, as a result of the effect of such elements as nickel and manganese in lowering the critical ranges. The diagram has been reproduced according to the usual form with the exception that the line *SE* has been drawn to corre-

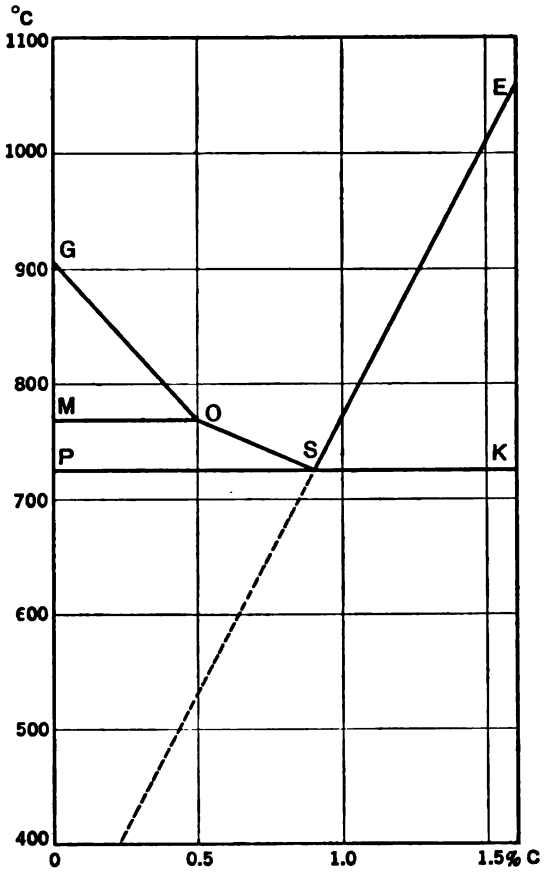

FIG. 10.—IRON-CARBON EQUILIBRIUM DIAGRAM, SOLID PHASES.

spond with the independent observations of Tschischewsky and Schulgin[18] and Saldaou and of Goerens[18] and extended below A_1. Any lowering of the line *GOS* will cause a corresponding displacement of the eutectoid composition, provided the line *SE* is not likewise shifted. The curves given in Fig. 8 indicate that the temperature difference, $A_3 - A_1$, will diminish to zero in a 0.40 per cent. carbon steel with a nickel content of approximately 12 per cent. Hence such a steel should be of eutectoid composi-

[18] Tschischewsky and Schulgin: *Jnl.* Iron and Steel Inst. (1917) **95**, 189. Saldaou and Goerens: *Rev. de Met.* (1917) **14**, 65.

tion, but this cannot be verified directly by experiment as a 12 per cent. nickel steel is not pearlitic on slow cooling. It is of interest to note that 12 per cent. nickel would hypothetically lower Ar_1 to 415° C., which is in close proximity to the line SE extended.

On the basis of the preceding considerations, it may be stated that the eutectoid composition is lessened by an amount equal to 0.042 per cent. carbon for each 1 per cent. nickel present, which agrees very closely with Bullens.[14] Using this value in connection with the curves of Fig. 9, good approximation can be made of the effect of carbon, the nickel remaining constant, on the critical ranges by moving these curves to the

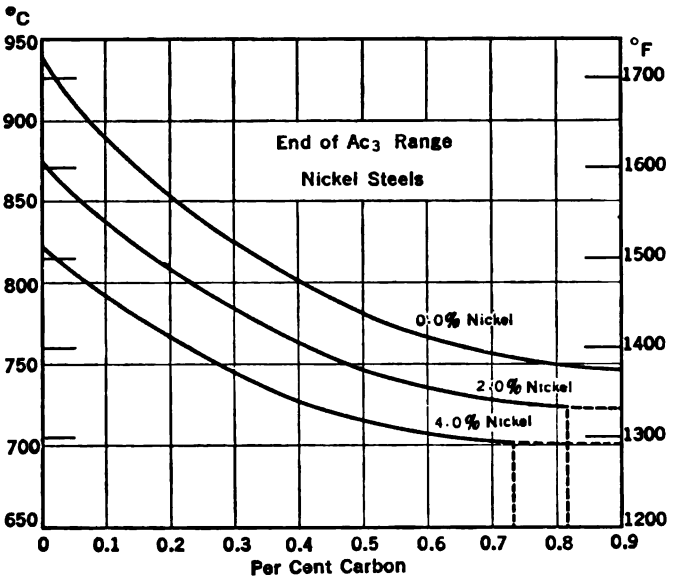

FIG. 11.—EFFECT OF CARBON ON END OF Ac_3 FOR 0, 2 AND 4 PER CENT. NICKEL.

left to correspond with the nickel content and down in proportion to the lowering effect of that content on Ac_1, as given in Fig. 8. This has been done in Fig. 11, the curves of which show the effect of carbon for 0, 2, and 4 per cent. nickel (the last nickel content is extrapolated) on the end of the Ac_3 range, except, of course, near the eutectoid compositions where the curves represent the end of Ac_1. The justification for these idealized curves lies in their agreement with Honda's values of Fig. 1 for zero carbon and with the values here given for 0.40 per cent. carbon and for the eutectoid composition as represented by the Ac_1 transformation.

The temperatures given for the end of the Ac_3 ranges do not, of course, represent practical heat-treatment temperatures. These values are only a basis from which to estimate the proper hardening or annealing tem-

[14] Bullens: "Steel and Its Heat Treatment," 304. John Wiley and Sons, N. Y.

perature for a given composition, which temperature is influenced under operating conditions by the mass of the steel to be treated and by the time it is subjected to the furnace temperature. The increase in hardening temperatures necessitated by these factors is sufficient to give a steep enough temperature gradient in the specimen being hardened by the time the Ar transformations are reached to insure thorough hardening. There is, however, no general rule which covers the effect of mass and time.

The foregoing discussion has been on the basis of material of known composition. When, however, the composition is only known to be within the limits prescribed by certain specifications, allowance may be necessary for the variation of carbon within these limits, which is usually ± 0.05 per cent. carbon. This variation amounts to 15–20° C. for a carbon content of 0.40 per cent. and is increasingly larger for lower carbons, as Fig. 11 clearly shows. This would indicate that for uniformity of product, the allowable variations in carbon content should be kept quite low; at least, for steels of lower carbon contents. This use of too wide allowable limits in the specification of carbon contents often leads to non-uniformity of product or much needless testing. Recently, for example, one of the government departments has had to resort to testing a considerable quantity of formed bars for the purpose of classifying them into smaller groups, according to the carbon content.

It might be noted, with regard to this problem of classifying nickel steels, that the thermal curves offer an accurate criterion for the carbon and nickel content of nickel steels, assuming other things are constant, as there is only one carbon content for a given difference between A_3 and A_1 and for one nickel content, which corresponds to a given temperature of A_1. The position of Ar_1 is of considerable commercial value in that it indicates the highest temperature at which the annealing operation can be arrested to substitute a more rapid cooling, thereby increasing the furnace output.

Summary

The following conclusions were drawn from a survey of the work of previous investigators of nickel steels:

1. The critical ranges Ac_3 on heating nickel steels have not been determined with as high a degree of accuracy as their industrial importance deserves.

2. The critical range Ar_3 and Ar_{3-2} on cooling iron-nickel alloys is lowered nearly linearly to absolute zero for about 34 per cent. nickel.

3. The critical range Ar_1 and Ar' of the pearlitic nickel steels is lowered with increasing nickel until the region of complete martensitization is reached when the transformation Ar'' alone is found at a much lower temperature.

The critical ranges were determined for six commercial nickel steels of 0.30 to 0.40 per cent. carbon, 0.55 to 0.75 per cent. manganese, 0.15 to 0.30 per cent. silicon content and nickel varying from 0 to 3.5 per cent., together with a pure iron-carbon alloy of 0.40 per cent. carbon content. They appear to warrant the following conclusions:

1. The point on the thermal heating curve designated as the end of Ac_3 is the fundamental criterion of heat-treatment temperatures, it represents the temperature at which all the ferrite is in solution, as determined by quenching tests.

2. The Ac_3 range is shown most sharply on the thermal curves at slow rates of heating.

3. The effect of the usual proportions of manganese and silicon on the Ac ranges is slight.

4. Rate of temperature change has only a moderate effect on the temperature of the transformations over the range investigated.

5. The position of the Ac ranges is more consistent than the Ar, due in part, at least, to the slighter effect of the previous structural condition.

6. The Ac_2 transformation is evident only in the two steels not containing nickel, which are of 0.40 per cent. carbon content, and is lower in the one containing appreciable amounts of manganese and silicon. A recalescence also is observed only in these steels.

7. Ac_1 is lowered by 10.5° C., Ar_1 by 21.5° C., and the eutectoid ratio is decreased by, approximately, 0.042 per cent. carbon for each 1 per cent. nickel added.

The data given supply a basis for the direct specification of thermal-treatment temperatures of 0.40 per cent. carbon, 0 to 4 per cent. nickel steels. Using the Ac_3 range of carbon steels as a basis, an approximation is obtained of the effect of variable carbon, with nickel constant. The effect of mass and time of heating must be considered in applying these data. The 0.05 per cent. carbon variation allowed in most nickel-steel specifications corresponds to a considerable variation in the Ac_3 range, particularly for low-carbon contents.

The author is indebted to Misses H. G. Movius and P. L. Thompson for their competent aid in the experimental work.

Static and Dynamic Tension Tests on Nickel Steel*

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(New York Meeting, February, 1921)

THIS investigation was undertaken to determine, if possible, the relation between static and dynamic tensile tests as measured by the work required to break test specimens slowly, in a tensile testing machine, and rapidly, by means of a falling weight. It was hoped that the investigation would throw some light on the role played by ductility under different rates of application of load.

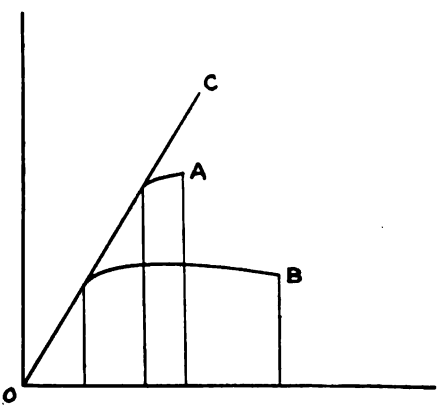

FIG. 1.—STRESS-STRAIN DIAGRAM.

In problems of design, it is usually assumed that the moduli of elasticity of all steels are equal; viz., about 30,000,000. The stress-strain diagram within the elastic limit is a straight line, as shown in Fig. 1, where *OA* is the curve of a hard steel and *OB* that of a soft steel. If the modulus of elasticity is constant, as assumed, the slope of the line *OC*

* The investigation here reported was carried out in the early part of 1915 at Watertown Arsenal, Watertown, Mass., when the authors were, respectively, Officer in Charge of the Laboratory, and Metallurgical and Testing Engineer. The report is now made public with the approval of the Ordnance Department, U. S. Army.

† Manager, Fiber Can Division, American Can Co.

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is constant. Therefore, whether a steel is dead soft or glass hard, the same load will always elongate it the same amount below the elastic limit. Also, as the area under the curve in the stress-strain diagram represents work done, the hard steel requires more work to stress it to its elastic limit than does the soft steel.

As a liberal factor of safety on the elastic limit is always used in designing, the question arises: "Why not use hard steel rather than soft and thus obtain the advantage of the higher elastic limit?" The answer usually given is: "Because the hard steel is brittle and will not resist shock." Experience shows that the more ductile a steel is, the more able it is to resist shock; impact tests on the Charpy impact testing machine confirm this. In most engineering work, however, the factor of safety is so liberal that it does not seem possible to stress the metal beyond its elastic limit. In that case the ductility would not appear to be important, because it does not come into play until the elastic limit is passed. If the elastic limit were passed, a permanent set would result which would disturb the equilibrum of the structure.

In the stress-strain diagram, the work done up to the elastic limit will be called the hypo-elastic work; and that done between the elastic limit and the point of rupture, the hyper-elastic work. In the static tensile test, it is evident that the hypo-elastic work is greater for hard steel than for soft, and the hyper-elastic is probably less for hard steel.

The experiments described were made in an effort to obtain answers to the following questions: Is the total work of rupture more or less for the hard steel? How is the total work of rupture affected by the speed of testing; that is, by the rate of application of load? Is the modulus of elasticity constant for all steels? Does ductility have any effect whatever below the elastic limit in the dynamic test?

Five pieces of nickel steel, 0.505 in. (12.8 mm.) in diameter and 10 in. gage length, containing 0.42 per cent. carbon, 0.48 per cent. manganese, 0.09 per cent. silicon, 0.035 per cent. sulfur, 0.035 per cent. phosphorus, and 3.20 per cent. nickel, were prepared as follows: One piece was annealed, one was oil hardened, and three were oil hardened and drawn to different degrees. These five pieces, representing steels of varying hardness, were then tested slowly in tension and the stress-strain diagram plotted. Five similar pieces were also tested in an impact machine with a recording device for drawing the stress-strain diagram. As the ductility varied in the five specimens, it was hoped to find the effect of this variation under static and dynamic loads.

Description of Impact Machine

A general view of the impact machine as arranged for this test is given in Fig. 2. The tup *A*, weighing 960 lb. (435 kg.), is connected to

the crosshead B by the test specimen C. The test is made by raising the crosshead and tup to the upper position and then releasing a hydraulic clutch K, causing the crosshead, tup, and test specimen to fall as one unit. After falling 4.5 ft. (1.35 m.) the crosshead B strikes the stops S but the tup A continues to fall, due to its inertia, and the test specimen is broken in tension by a suddenly applied load. A pencil P attached to

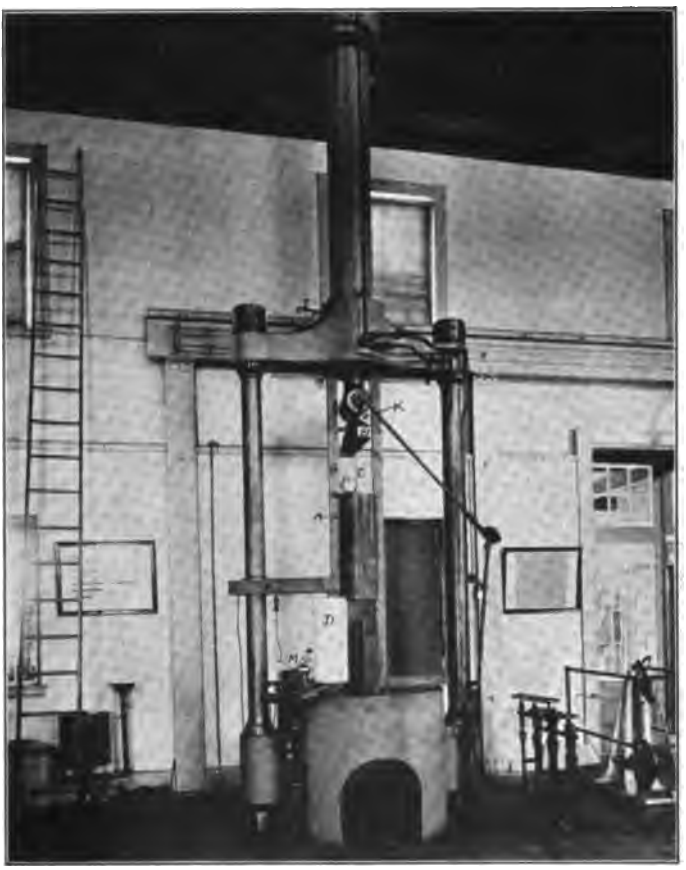


FIG. 2.—GENERAL VIEW OF IMPACT MACHINE.

the tup A describes a curve on a revolving drum D, the surface speed of which is determined from a sine curve described by a small motor M.

Fig. 3 shows the details of the recording mechanism. The pencil P is shown in contact with the drum D and the sine curve is shown faintly at X. The weight A falls between the guides G, and when the pencil P comes into contact with the revolving drum D it describes a curve Fig. 4 shows a side view of the recording apparatus. The motor Y

drives drum D; the curve described by the falling weight is shown faintly at Z.

The time-recording motor M is operated as follows: At a certain point in the descent, a brass strip attached to the falling weight makes contact with two other brass strips R, thus completing a circuit through a magnet placed just behind the end of a stylus attached to the shaft

FIG. 3.—FRONT VIEW OF RECORDING APPARATUS.

of motor M through a connecting rod; this causes the stylus to move sharply over and make contact with the drum D. As the motor M revolves, the stylus is given a rapid reciprocating motion in a vertical plane. This vertical motion, combined with the horizontal motion of the drum, produces a sine curve from which, the revolutions per minute of the motor M being determined, the surface speed of the drum D can

be calculated. The length of the brass strips R is such that the stylus is in contact with the drum for only one-half a revolution of the drum.

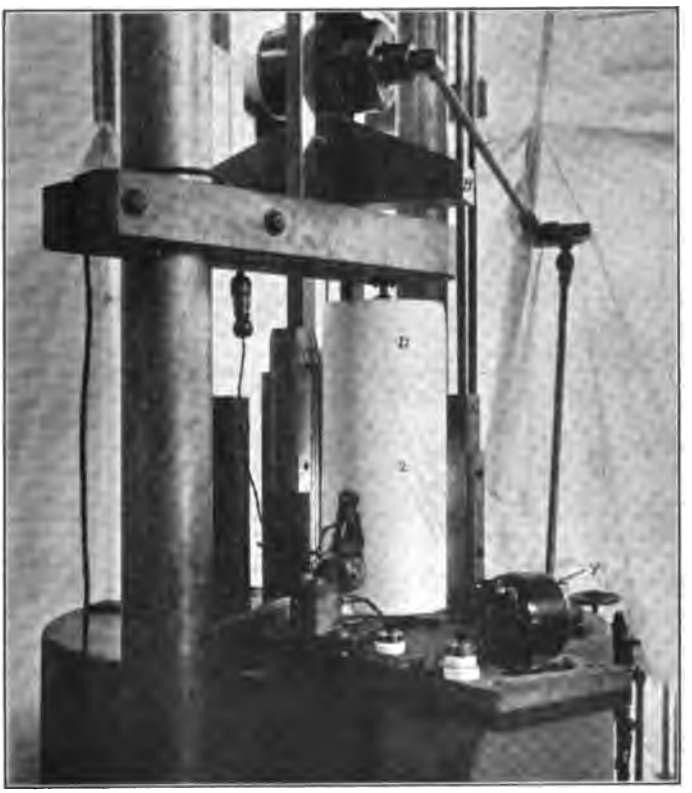


FIG. 4.—SIDE VIEW OF RECORDING APPARATUS.

DESCRIPTION OF CURVES

With the test specimen in place and the crosshead B resting on the stops S, the pencil P is allowed to touch the revolving drum, thus tracing the datum line OO'; any subsequent motion of the pencil below this line represents an elongation of the test specimen. The entire system is then raised about 3.5 ft. and released by the hydraulic clutch. During the fall, the pencil records on the revolving drum a parabola of free fall until the crosshead B meets the stops S. At this point the reaction of the test specimen retards the falling weight and the curve becomes concave upwards until the specimen breaks, after which the curve is another parabola of free fall. It is desired to determine the work required to break a specimen under impact. For purposes of illustration, the work from data on the curve for test bar No. 1, Fig. 15, is calculated.

The motor M made 6700 r.p.m. By measuring the distances on the sine curve and using the formula $V = \frac{S}{t}$ the surface speed of the drum

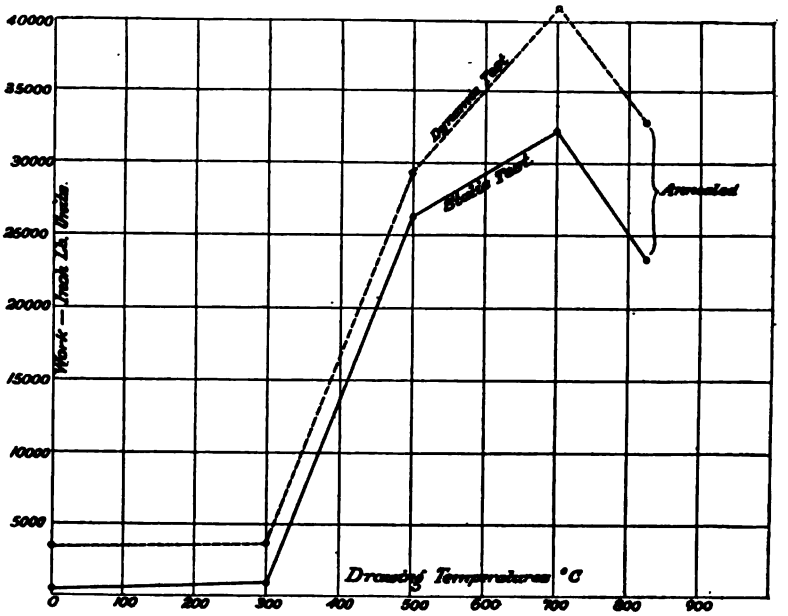


FIG. 5.—WORK CURVES.

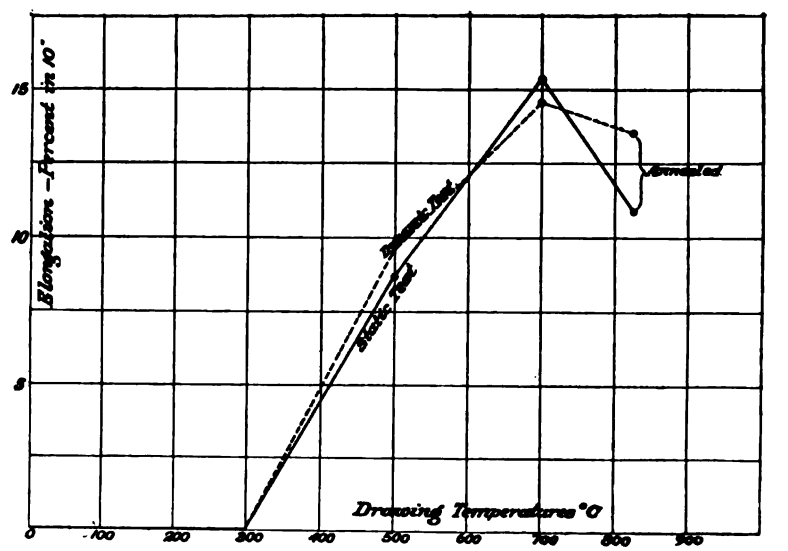


FIG. 6.—ELONGATION CURVES.

was found to be 147.6 in. per sec. By taking the horizontal and vertical components of the tangent to the curve at the point where it crosses

the datum line OO', the velocity of the falling weight at the instant the load was applied was found to be 201.8 in. per sec. The horizontal component was the velocity of the surface of the drum. The kinetic energy of the system was therefore $\frac{1}{2}MV^2 = \frac{1}{2} \times \left(\frac{960}{32.2 \times 12}\right) \times (201.8)^2$. This gives the actual energy in the system at this instant, and eliminates the question of friction of guides, air, etc.

By drawing a tangent at a point 5 in. (12.7 cm.) below the datum line, OO' the vertical velocity is found to be 134.9 in. per sec. The energy absorbed by the test specimen is, therefore,

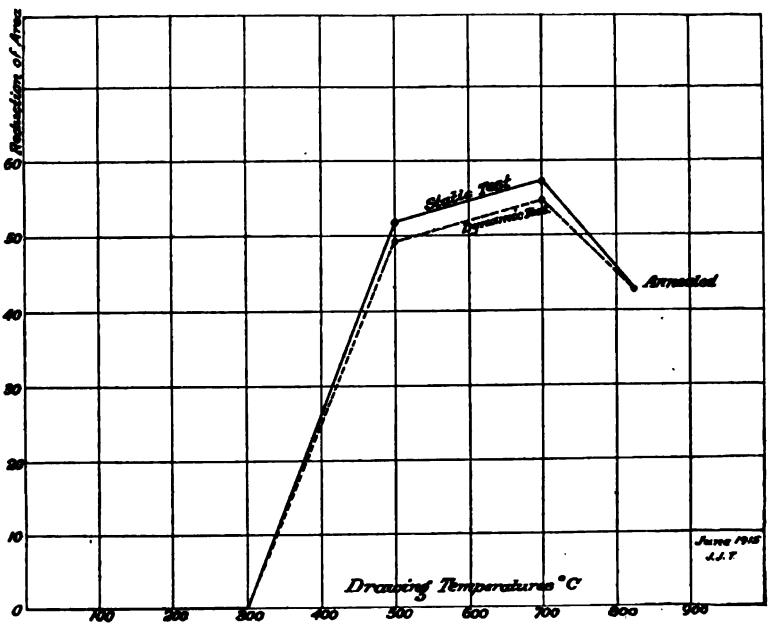


FIG. 7.—REDUCTION OF AREA CURVES.

$$E = \tfrac{1}{2}MV_1^2 + Wh - \tfrac{1}{2}MV_2^2 = \tfrac{1}{2}M(V_1^2 - V_2^2) + Wh$$
$$= \tfrac{1}{2} \times \frac{960}{32.2 \times 12} \times (\overline{201.8^2} - \overline{134.9^2}) + (5 \times 960)$$
$$= 32{,}830 \text{ in.-lb.}$$

where

V_1 = velocity at OO';
V_2 = velocity 5 in. below OO';
W = weight = 960 lb.;
h = 5 in.;
M = mass = $\frac{W}{32.2 \times 12}$

The elongation was found to be 13.5 per cent. for a 10-in. (3-m.) gage length, or 1.35 in. By laying off this distance as indicated, the time the load was on the specimen was found to be 0.008 second.

Discussion of Results

Tables 1 and 2, and Figs. 5 to 8 summarize the results obtained. The curve in Fig. 5 indicates that more work is required to break a specimen under a rapidly applied load than under one slowly applied. Nickel steel that has been quenched but not drawn, or drawn up to 300° C. is very brittle, and required very little work to break it under either a rapidly or slowly applied load.

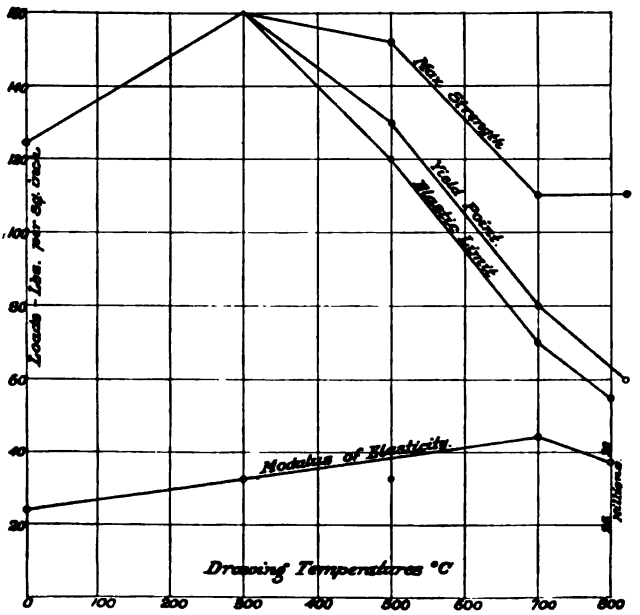


Fig. 8.—Static test.

The curves shown in Figs. 6 and 7 indicate that the ductility is independent of the rate of application of the load. As work is the product of force and distance, we must conclude that as the elongation is the same and the work is greater, the resisting force of the metal is greater for suddenly applied loads.

The curves shown in Fig. 8 indicate that for a slowly applied load this metal was hard and brittle when drawn at temperatures of 300° C. or lower. Beyond this point, however, a real softening effect is obtained. For low drawing temperatures, the maximum strength, yield point, and elastic limit, or limit of proportionality, occur at the same point, thus

TABLE 1

	Static Test					Dynamic Test				
	Annealed	Drawn at Degrees C.				Annealed	Drawn at Degrees C.			
		700	500	300	0		700	500	300	0
Work, in.-lb. units	22,435	32,227	26,133	873 963	598	32,830	41,300	29,300	3679	3538
Elongation, per cent	10.9	15.3	8.7	0	0	13.5	14.6	9.6	0	0
Reduction of area, per cent.	40.3	57.2	51.9	0	0	40.3	54.6	49.1	0	0
Hardness	202	228	321	477	600	202	228	321	460	600
		Approximate time								
Time of load	20 min.	20 min.	20 min.			0.0080 sec.	0.0099 sec.	0.0073 sec.	0.0 sec.	0.0 sec.
Velocity of impact, in. per sec	Very slow					201.8	197.4	180.8	201.9	174

TABLE 2.—*Static Test*

	Drawn at 700° C.	Drawn at 500° C.	Drawn at 300° C.	Drawn at 0° C.	Annealed at 825° C.
Maximum load, lb. per sq. in.	110,000	152,000	156,500 165,500	124,500	110,000
Elastic limit, lb. per sq. in.	70,000	120,000	156,500 165,500	124,500	55,000
Yield point, lb. per sq. in...	80,000	130,000	156,500 165,500	124,500	60,000
Modulus of elasticity.....	31,000,000	28,200,000	28,200,000 28,500,000	26,100,000	29,400,000

giving a brittle steel that fails without warning. This may be due to internal strains that have not been removed, or to the hard martensitic structure of the steel. For higher drawing temperatures there is a marked increase in the ductility, as indicated by the curves in Figs. 6 and 7, and a greater resistance to shock, as indicated by the curve in Fig. 5.

CONCLUSIONS

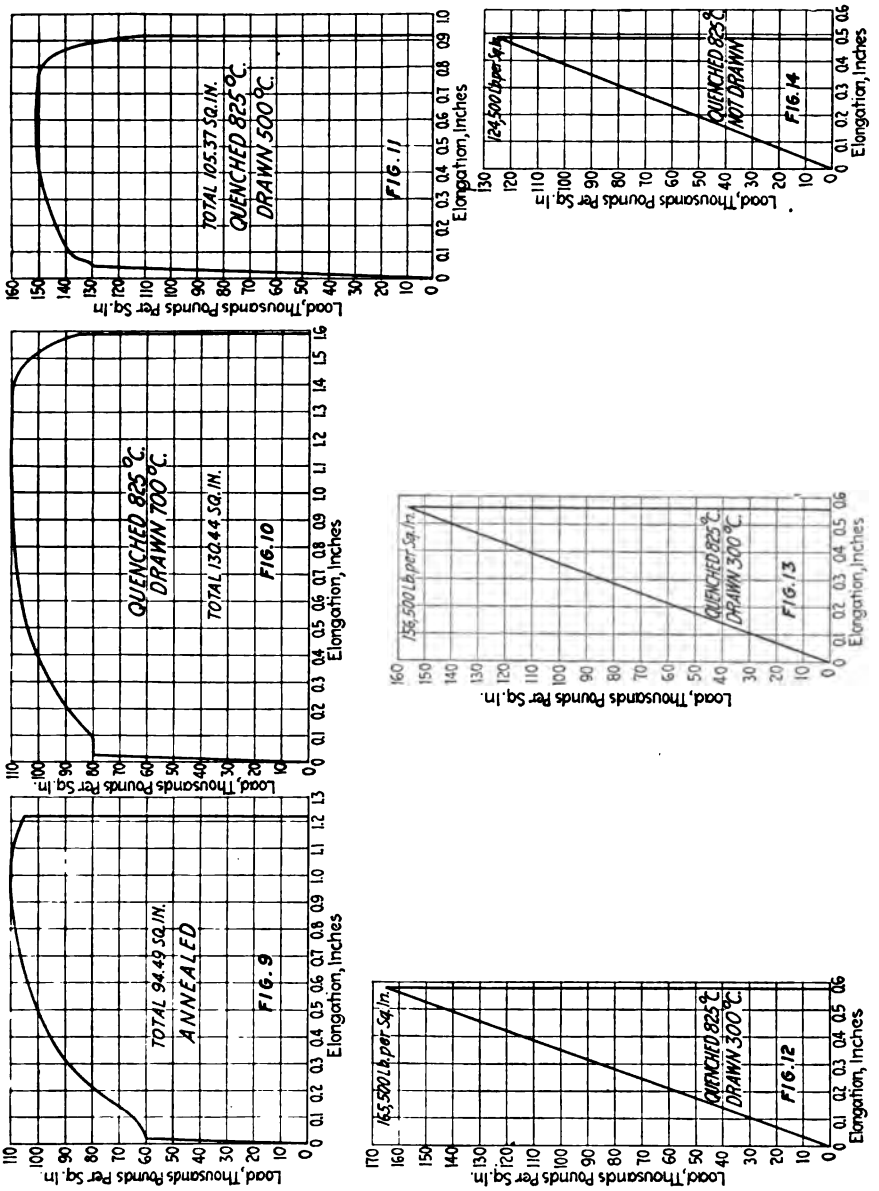
1. The curve in Fig. 5 indicates that for hard steels the total work of rupture is very low under either a slowly or a rapidly applied load.

2. The curve in Fig. 8 indicates that the modulus increases slightly with the higher drawing temperatures; this increase is probably too slight, however, to have a commerical value.

3. If we could be absolutely sure that the applied stresses would never exceed the elastic limit, and that the steel would never be subjected to a live load, we could use a hard steel, and with a smaller area obtain the resisting force of a soft steel, due to the higher elastic limit. In most problems of design, however, live loads will be encountered, either during the fabrication of the material or in service. The curve shown in Fig. 5 proves conclusively that hard steels require little work for rupture; therefore, any small suddenly applied load would be sufficient to cause fracture.

4. The curves in Figs. 5 to 7 indicate that for the low drawing temperatures both the ductility and the work of rupture are very low. As ductility increases, the work of rupture increases. For hard steels, therefore, a force, less than the elastic limit, if applied with sufficient velocity, will develop enough kinetic energy to cause rupture. For example, the curve in Fig. 8 shows that for a drawing temperature of 300° C. the elastic limit is 160,000 lb. per sq. in. (11,248 kg. per sq. cm.); while the curve in Fig. 5 shows the work of rupture to be only 3679 in.-lb. By calculation, it is found that a load of 80,000 lb. per sq. in., or one-half of the elastic limit, if dropped from a height of 0.046 in. will cause rupture.

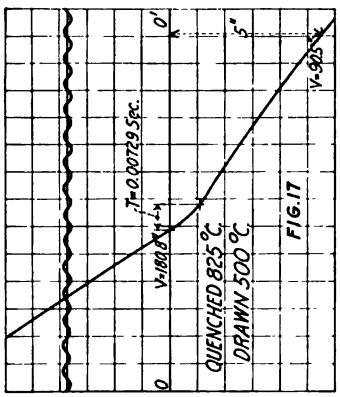
It is evident, therefore, that force alone is not the proper criterion by which to measure the strength of material. The work unit is more valuable as a measure of strength, and as ductility is an indication of

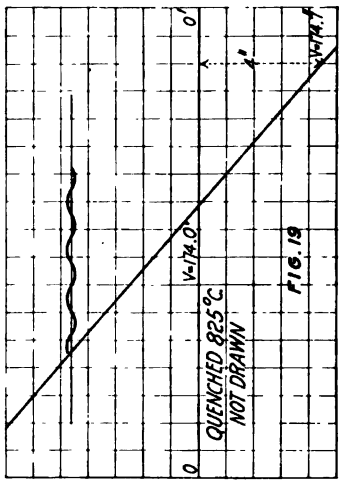


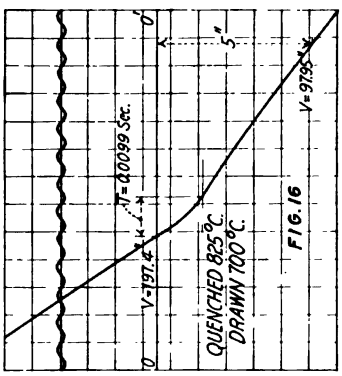
the work required to rupture, it is wise to specify a high ductility for all parts subject to shock.

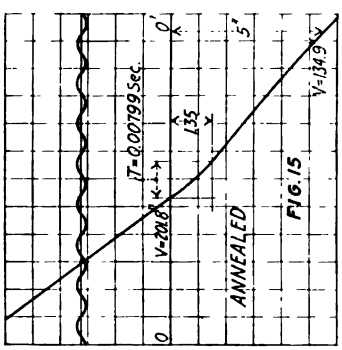
Ductility, as measured by elongation and reduction of area, in the ordinary tension test, is important, therefore, not for the part it itself

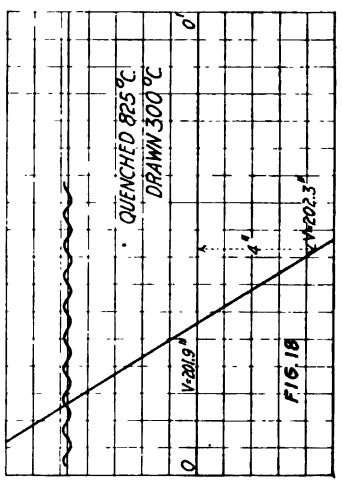
plays but as an indication of strength as measured by work units. The curves in Figs. 5 to 7 indicate that steel is in its best condition when quenched and drawn just under its critical temperature.











The curves given in Figs. 9 to 19 illustrate the type of curve obtained for the various heat treatments, for both static and dynamic loading. The work of rupture for the static tests was obtained by measuring the area under the stress-strain curve by means of a planimeter.

Fig. 9 shows the stress-strain diagram for the static tension test on annealed test bar No. 3: elongation was 10.9 per cent.; cont., 40.3 per cent.; work, 23,435 in.-lb.; E = 29,400,000. The stress-strain diagram of the static tension test on specimen No. 6, which was quenched at 825° C. and drawn to 700° C., is shown in Fig. 10: elongation was 15.3 per cent.; cont. 57.2 per cent.; work, 32,227 in.-lb.; E = 31,100,000. The stress-strain diagram for the static tension test of test bar No. 9, which was quenched at 825° C. and drawn to 500° C., is shown in Fig. 11: elongation was 8.7 per cent.; cont., 51.9 per cent.; work, 26,133 in.-lb.; E = 28,200,000.

Fig. 12 shows the stress-strain diagram for the static tension test on test bar No. 11, which was quenched at 825° C. and drawn to 300° C.: elongation was 0; cont., 0; work, 963 in.-lb.; E = 28,500,000. The stress-strain diagram for the static tension test on test bar No. 12, which had the same treatment as bar No. 11, is shown in Fig. 13: elongation, 0; cont., 0; work, 873 in.-lb.; E = 28,200,000. Test bar No. 15 was quenched at 825° C. but not drawn. The stress-strain diagram for the static tension test shown in Fig. 14 shows that the elongation was 0; cont., 0; work, 598 in.-lb.; E = 26,100,000.

Fig. 15 shows the curve of the dynamic test on bar No. 1, which was annealed. The tup dropped 4.5 ft., the speed of drum was 147.6 in. per sec., and the speed of motor was 6700 r.p.m.; elongation was 13.5 per cent.; cont., 40.3 per cent.; work, 32,830 in.-lb.

Fig. 16 shows the curve of the dynamic test on bar No. 5, which was quenched at 825° C. and drawn to 700° C.; elongation was 14.6 per cent.; cont., 154.6 per cent.; work, 41,300 in.-lb. The motor speed was 8588 r.p.m., the speed of the drum was 128.3 in. per sec., and the drop of the tup was 4.5 ft. Fig. 17 shows the curve of the dynamic test on bar No. 14, which was quenched at 825° C. and drawn to 525° C.; elongation was 9.06 per cent.; cont.; 49.1 per cent.; work, 29,300 in.-lb. The motor made 8040 r.p.m. and the speed of the drum was 115.2 in. per sec. The curve of the dynamic test on bar No. 16, which was quenched at 825° C. and drawn to 350° C., is given in Fig. 18; elongation was 0; cont., 0; work, 3979 in.-lb. The motor made 7360 r.p.m. and the drum speed was 124.7 in. per sec. Fig. 19 shows the curve of the dynamic test on bar No. 15A, which was quenched at 825° C. and not drawn; elongation was 0; cont., 0; work, 3538 in.-lb. The motor made 7400 r.p.m. and the speed of the drum was 198.3 in. per sec.

DISCUSSION

H. D. HIBBARD, Plainfield, N. J.—The question of the work required to break a test piece depends on what has been called the merit number; that is the number obtained by multiplying the tensile strength, in pounds, by the elongation, in inches. That number will show that the

soft steels have a much higher merit number than the hard steels, and it corresponds with the difficulty of breaking the piece of soft steel as compared with that of hard steel. There is a variation of that merit number; instead of multiplying the tensile strength by the elongation, the elastic limit is multiplied by the contraction of area; the results are quite similar.

GEORGE F. COMSTOCK, Niagara Falls, N. Y. (written discussion).—The paper brings out clearly the necessity for some ductility accompanying a high elastic limit in structural steels, but it does not state that "ductility as measured by elongation and reduction of area in the ordinary tension test" is not sufficient alone to insure good resistance to shock. It was shown by S. L. Hoyt[1] that two specimens of steel may have practically identical elongation and reduction of area in tension, and yet one may be much more easily broken by impact than the other. The case of soft steel castings is quite familiar; it is well known that they show good ductility in tension when not annealed, and yet have low shock resistance in an impact test unless heat-treated in some way, although the heat treatment may not be necessary at all for passing tensile-test specifications. Thus, it seems unfortunate that the impression should be given by this paper that good resistance to shock may be insured in all cases merely by obtaining high ductility in tension. This may be true for certain grades of steel, but it has been shown to be an unsound idea for general application. In order to get a reliable measure of shock resistance, some form of impact test should be used, rather than trusting solely to the ductility shown in tension.

A. G. ZIMERMANN,* (written discussion).—The curves contain an excellent summary of the results obtained and Figs. 9 to 19 are exceedingly instructive. The curves of static work have been based on the work done on the specimens up to the moment of rupture. The curves of dynamic stresses, on the contrary, represent work done by the specimen and by the 960-lb. tup through an apparently arbitrary space of 5 in. The work recorded as done by the specimens in dynamic test is, therefore, somewhat in error, and as this error is not constant the results are not exactly parallel with true conditions.

Fig. 15 shows that after the specimen is broken, the tup overcomes the deceleration caused by the specimen, begins to accelerate uniformly (the curve again becomes a parabola), and gains the velocity noted at 5 in. from the stop. As the elongation of the specimens differs, as well as the decelerations they cause, the error in taking the residual velocity at 5 in. is variable.

For the purpose of illustration, the writer has endeavored to analyze the curve in Fig. 15, and has calculated the residual velocity at the

[1] Static, Dynamic, and Notch Toughness, *Trans.* (1920) **62**, 485, Table 1.

* Lieutenant Commander, U. S. Navy.

moment of rupture (1.35 in.). By the same means, the velocity at 5 in. was calculated to be 136.8 in. per sec., as compared to the authors' 134.9 in. per sec., showing the results to be near enough to permit of discussion based on them. The velocity at the moment of breaking, then, was found to be 127.2 in. per sec. The equation

$$E = \frac{1}{2} \times \frac{960}{32.2 \times 12} \times (201.8^2 - 134.9^2) + (5 \times 960) = 32{,}830 \text{ in-lb.}$$

would then become

$$E = \frac{1}{2} \times \frac{960}{32.2 \times 12} \times (201.8^2 - 127.2^2) + (1.35 \times 960) = 31{,}795 \text{ in-lb.}$$

Even with this corrected method, the work done on dynamic specimens of this grade of steel will generally be somewhat greater than on static, so the conclusions drawn from Fig. 5 are, in general, correct. But what does an expression for the dynamic strength of steel in inch-pounds mean to the average business man who wishes to buy material? His ideas of strength of material under any conditions turn instinctively to the units expressing static strength that have been used for generations. But if he is given an expression, in pounds per square inch of original area, that will be a close approximation of the stress on the specimen at the moment of breaking, he has something that he can understand and can compare with statistics in any handbook.

The writer does not believe that an expression in pounds per square inch is impossible to arrive at. In a discussion read before the Institute, at its Chicago meeting in September, 1919, he suggested that such units were feasible and outlined a method of computing them. The evaluation in the case under discussion is comparatively simple, being

$$\text{Stress} = \text{Force} + \text{Weight}$$

$$= \frac{960}{32.2 \times 12} \times (201.8 - 127.2) + 960 = 1144.8 \text{ lb. or } 5724 \text{ lb. per sq. in.}$$

This is determined as follows (see Fig. 15):

$F = M\alpha$

M = mass of W, 960 lb. tup.

$\alpha = V_a - V_b$ = deceleration (minus acceleration) caused by specimen.

$S_1 = F + W$

V_a = velocity at OO'

V_b = velocity at 1.35″

S_1 = total stress on specimen at moment of rupture, when it is supporting (or just failing to support) weight W.

A similar piece of steel, in these experiments, had a maximum static strength of 110,000 lb. per sq. in. and its dynamic strength is 5,724 lb.

per sq. in. These figures closely approximate the stress on these specimens at the moment of rupture, referred to the original cross-sectional area of the specimen, and identical results (within the limits of experimental error) will be obtained from identical material under the same conditions of test.

It is earnestly hoped that this country will take the lead in breaking away from the mysterious foot-pound notched-bar units inherited from foreign countries and will adopt a standard test that gives a result that looks rational to the buyer and user of material and is a true index of what the material has resisted under impact under standard conditions. To accomplish this, it is but necessary to determine the best height of fall and weight for all metals or to assign two standards, one for ferrous and one for non-ferrous metals, as experiment proves wisest. The adoption of such standards will be met with popular appreciation and will consign the comparatively few statistics in inch-pound, foot-pound, multi-standard units to the realm of purely technical research.

J. H. NEAD (author's reply to discussion). The first sentence at the top of page 128, "The curves in Figs. 5 to 7 indicate that steel is in its best physical condition when quenched and drawn just under its critical temperature," is meant to convey the idea that steel is in its best physical condition for maximum strength, ductility, and resistance to shock when it has been quenched from just above the A_3 point and reheated or drawn back to just below the A_1 point.

We agree with Mr. Comstock that ductility alone is not sufficient to insure the best resistance to shock. We know of other cases than the one mentioned by Mr. Comstock where steel gave practically identical results on the tension test in both the annealed and heat-treated conditions, but results obtained on the Charpy impact test showed the heat-treated material to be much superior to the annealed material in its shock-resisting qualities. We believe, however, that good ductility on the tensile test does imply fairly good shock resistance. This is borne out by many laboratory tests made by the writer as well as by the published results of others.

We are pleased to learn that Mr. Zimmerman's corrected method of calculating the work done on the specimens in dynamic tests verified the conclusions we had reached.

The Coefficient of Expansion of Alloy Steels

By John A. Mathews,* Ph. D., Sc. D., Syracuse, N. Y.

(New York Meeting, February, 1920)

During the prosecution of the aircraft-production program in 1917 and 1918, the writer visited many plants engaged in the manufacture of motors, planes and parts, in carrying out his duties as chairman of the Committee on Aircraft-engine Forgings. On several occasions, when the question of expansion was discussed, it was noted that there was confusion in the use of the terms: the true coefficient of expansion, a physical constant, and distortion in hardening. One engineer, referring to a steel shown in the accompanying table, stated that he could not consider it for crankshafts because of its excessive coefficient of expansion, while another steel, also listed in the table, was said to be especially good because it had no coefficient of expansion, since it came out of the oil bath perfectly straight. Many years ago one of our employees designed a new oil furnace; when asked what became of the products of combustion, he replied: "There ain't any, we burn them all up."

While the coefficient of expansion is not without its effect in volume changes in hardened steel, it is not a determining factor in the matter of distortion and going out of shape. Irregular heating, uneven furnace bottoms, and carelessness in withdrawing the part from the furnace, as well as the manner in which the part enters the quenching bath are of greater moment. Generally speaking, also, steels of relatively low hardening temperature will distort less than those requiring higher hardening heats. The coefficient of expansion must be considered in engineering design most frequently when different metals or alloys are used in the same construction. For example, the difference of expansion between a steel crankshaft and an aluminum crank case might be of real importance and a steel with no coefficient of expansion would be much less desirable than one with the normal coefficient.

About 15 years ago, the writer made many determinations of the coefficient of expansion at low temperature ranges, usually between 20° and 100° C. Among the materials tested were: Pure forged electrolytic iron, 11.73 parts per million for 1° C.; cast aluminum (99.93 per cent. Al.),

* President, Halcomb Steel Co.

23.86; monel metal, 13.75; nickel steel (30 per cent. Ni.), 13.38; soft steel, 11.09; commercial nickel, 12.42. These figures illustrate a general defect noticeable in much of the published data, namely, complete analyses and conditions of heat treatment are frequently lacking. For example, the following values are taken from tables of physical constants: Soft iron, 12.10; wrought iron, 11.40; steel, annealed, 10.95; steel, 13.22; nickel, 12.79; cast brass, 17.22; tempered steel, 12.40.

Most of these materials may represent a wide variety of analyses and a wide variety of physical conditions, and a comparison of various tables from different sources would lead one to suspect that there was likely to be some variation in the constants of nature. Few laboratories are equipped to make these tests and, at least until very recently, there has not been available any commercial form of dilatometer that could be used by the average laboratory worker. It would not be necessary for every laboratory to make these determinations if the full information were available in connection with the determinations that have already been made by many able investigators.

Through the coöperation and assistance of Major Heaslet and Capt. H. F. Wood, of the Detroit Branch of the Aircraft Production Department, our committee was assisted in securing various types of alloy steels used for crankshafts; and in connection with them we have the analyses and tensile properties, also the hardness and shock-test values in several cases. The writer has supplemented this list with other types of alloy steels frequently used for axles, shafts, etc.; all of this material has been tested in a heat-treated condition, which has produced elastic properties between 100,000 and 150,000 lb. per sq. in. yield point. The Bureau of Standards coöperated with the committee and made the actual tests of coefficient of expansion, which is a sufficient guarantee of the accuracy of the figures presented. We hope the complete data presented may prove of value to engineers and that future authors, in presenting data on the same subject, may follow the example set. The accompanying table shows mark, analyses, tensile properties, hardness, Izod figures, and the coefficient of expansion for two ranges of heating; viz., 25° to 100° C. (77° to 212° F.), and 25° to 270° C. (77° to 518° F.), the steels being arranged in the order of increasing coefficients for the wider range of heating.

Where exact heat treatment is not given, we feel reasonably certain that the crankshafts were hardened from a temperature of about 1550° F. (840° C.) and quenched in water until black, after which they were immediately put into the drawing furnace and the temper drawn to about 1050° F. (570° C.). In a few cases it is possible that the original quenching was done in oil rather than in water.

It will be noted that the maximum variation between the highest and the lowest coefficient of this widely differing group of steels is only 1.34 parts per million for 1° C. Practically considered, there would be considerable difference between these steels as to their actual behavior on

TABLE 1

Mark	Analysis									Tensile			
	Carbon	Silicon	Manganese	Phosphorus	Sulfur	Chromium	Vanadium	Nickel	Molybdenum	Elastic Limit, Lb. per Sq. In.	Ultimate Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent., in 2 In.	Reduced Area, Per Cent.
WG12085...	0.34	0.10	0.64	0.012	0.023	0.76		3.43		122,500	142,750	17.9	57.0
Ford.....	0.30	0.11	0.66	0.025	0.005	0.86		3.05	0.53	135,700	149,000	19.0	63.0
PF16990....	0.50	0.15	0.64	0.015	0.031	0.88		1.90		124,300	140,600	20.0	56.4
X.....	0.32	0.23	0.53	0.013	0.015	1.37		3.53		145,000	154,000	19.5	60.95
6555.....	0.35		0.65	0.008	0.045	0.80		3.14		125,500	135,250	18.5	56.2
15772.....	0.43		0.78	0.015	0.027	0.75		1.87		129,650	147,400	18.5	57.7
16404.....	0.43	0.18	0.81	0.031	0.032	0.88	0.07	2.55		140,000	155,500	17.5	50.63
257.....	0.40	0.14	0.76	0.006	0.012	1.20	0.17			157,500	175,500	16.0	50.9
1048.....	0.34	0.17	0.72	0.009	0.010	0.96	0.17			119,000	135,000	20.0	59.95
1156.....	0.44	2.07	0.81	0.012	0.010					117,500	148,000	22.5	49.55
1223.....	0.40	0.57	0.78	0.011	0.015	0.78				90,000	118,500	20.5	58.9

Mark	Hardness		Impact Test	Coefficient of Expansion, Parts per Million per 1° C.		Source and Treatment
	Brinell	Shore	Izod	Range 25° to 100° C. 77° to 212° F.	Range 25° to 270° C. 77° to 518° F.	
WG12085..	311	51	56	11.37	12.49	Liberty shaft from Lincoln.
Ford.....	302	43	51	11.67	12.57	Liberty shaft from Ford.
PF16990...	302	50	49	11.72	12.70	Liberty shaft from Packard.
X.....	325			11.83	12.78	Quenched 1525° F. (830° C.) oil; drawn 1050° F. (570° C.).
6555.....				11.73	12.79	Liberty shaft, source unknown.
15772.....	302			12.00	12.87	Liberty shaft, source unknown.
16404.....	323			11.65	12.89	Rolls-Royce shaft.
257.....	370			11.60	13.04	Quenched 1700° F. (930° C.) oil; drawn 1200° F. (650° C.).
1048.....	282			11.76	13.10	Quenched 1700° F. (930° C.) oil; drawn 1150° F. (620° C.).
1156.....	318			12.52	13.51	Quenched 1700° F. (930° C.) oil; drawn 1100° F. (590° C.).
1223.....	237			12.76	13.83	Quenched 1525° F. (830° C.) oil; drawn 1100° F. (590° C.).

quenching in regard to the distortion which would take place, but this small difference in coefficient of expansion can hardly be considered as the cause of these differences. On the other hand, a tool-steel product introduced to the American trade by the writer's company many years before his connection with the company, is practically free from distortion in hardening and in volume change after hardening and tempering yet it displays a normal expansion upon heating, not differing in any way from that of plain carbon tool steel. It shows a greatly increasing rate of dilatation upon heating up to Ac_1, but then undergoes the usual marked contraction until decalescence is complete, followed by a new dilatation at a greater rate than that below Ac_1, which agrees perfectly with Le Chatelier's[1] observations upon the behavior of carbon steels referred to previously by the writer.[2] The fact that this product holds its shape more nearly than any other tool-steel product and undergoes almost no volume change when properly hardened, peculiarly adapts it to a wide variety of uses in the tool room and shop. That it met a pressing need is further shown by the fact that a steel of this type is now made by nearly every manufacturer of tool steel. As the writer was not connected with the original development of this product he may be pardoned if he expresses an opinion that its properties are of interest second only in importance to the invention of high-speed steel.

The low-carbon chromium-nickel steels undergo normal expansion on heating, yet in one instance fairly large and intricate gears for airplane use were made from this type of steel. They were so well handled, in the hardening and subsequent treatment, that they showed no warpage or distortion and required no straightening or grinding after the heat treatment. This result was due to the skill of the operator, as the gears were not hardened in dies or with a gear-hardening machine. As they were for airplane use, they were very light and of a construction very apt to cause trouble unless the greatest care was exercised in the treatment. This again illustrates the fact that the coefficient of expansion, in itself, is not a primary cause of distortion in heat treatment, although, in general, hardening from a temperature just about that at which the maximum contraction takes place at decalescence would tend to improve the final results of hardening so far as distortion is concerned; this practice is now in use in some progressive plants where the end of decalescence is directly determined from pieces in the furnace rather than by relying upon the reading of the pyrometer located at a more or less remote spot in the furnace.

[1] "Contribution à l'Étude des Alliages," 386.

[2] J. A. Mathews and H. J. Stagg: Factors in Hardening Tool Steel. *Trans.* Amer. Soc. Mech. Engrs. (1914) 845.

Molybdenum Steels

By John A. Mathews,* Ph. D., Sc. D., Pittsburgh, Pa.

(New York Meeting, February, 1921)

It is twenty years since the writer made his first molybdenum steels and others were making them commercially five years earlier but the prevailing opinion seems to be that molybdenum steels are new; from time to time the daily press speaks of important discoveries in Europe and intimates that American steel makers have much to learn in regard to alloy steels. The earlier experiments were largely confined to the use of relatively high percentages of molybdenum in tool steels and permanent magnet steels. Recent developments deal with the types of alloy structural steels used for airplane, automobile, and other engineering requirements; in these, the molybdenum content is usually less than 1 per cent. The earlier types generally have been unsuccessful commercially, but the newer types of steels are becoming of increasing importance.

The war showed our dependence on foreign sources for alloying metals; molybdenum alone is widely distributed in the United States and seemingly abundant. Many deposits are not now of commercial interest, owing to location and relatively small amount of ore available, but other deposits are being developed and a stable source of supply seems well assured.

In tool and magnet steels, it was early found that 1 part of molybdenum was equivalent to from 2 to 2.5 parts of tungsten. The permanent magnet steels investigated by Madame Curie,[1] in 1898, contained from 3.36 to 4.05 per cent. molybdenum; in 1902, Dr. E. L. French and the writer thoroughly tested steels containing from 2.0 to 4.0 per cent. These steels gave satisfactory tests for permanence, but were low in residual density and much more sensitive to hardening than the corresponding tungsten products. We discontinued work with them, therefore, and have no advice that such steels have been used commercially here or abroad.

Prior to the development of the Taylor-White process and the modern high-speed steels, air-hardening steels were in general use. These were

* President, Crucible Steel Co. of America.

[1] *Bull.* Soc. d'Encourage. l'Ind. Natle. (Jan., 1898).

high in carbon and usually contained tungsten and chromium, the latter having replaced the manganese of the original Mushet air-hardening steels. Later, the tungsten content was frequently replaced by molybdenum. An air-hardening steel largely used had the following analysis: carbon, 1.75 to 2.00 per cent.; molybdenum, 3.75 to 4.25 per cent.; chromium, 3.75 to 4.25 per cent.

In the earlier years of the twentieth century, high-speed steels quickly displaced the air-hardening steels. Most of the manufacturers confined their efforts to tungsten-chromium combinations, but in America determined efforts were made to use molybdenum instead of tungsten. At the time that one European metallurgist was claiming that steel containing over 6 per cent. molybdenum could not be rolled, we were commercially rolling large quantities of a steel containing over 9 per cent. molybdenum and had successfully rolled steel containing up to 15 per cent. The use of molybdenum above 6 per cent. was patented,[2] as was the use of vanadium with either tungsten or molybdenum in high-speed steel.[3] So far as molybdenum was concerned, the manufacture of these steels was discontinued almost before the patents had been allowed. One of these patents has now expired, but "discoveries" of chrome-molybdenum-vanadium steel and molybdenum-vanadium steel for high-speed purposes were recently announced. Both of these types of steels were made and abandoned nearly 20 years ago, as they were found, after very exhaustive experiments and tests, to be unsatisfactory both to manufacturer and in use. Occasionally these steels gave extraordinarily good service, as measured by the standards of that time, which were much below the present standards of the leading high-speed steels. However, notwithstanding the discouraging results of the earlier experiments, the writer has felt that some time we should have to use molybdenum, due to shortage of tungsten, or for other economic reasons, and from time to time during the past 20 years we have repeated our experiments with these steels, with the hope that the general advancement in the art of manufacture might help us to overcome the earlier difficulties and objectionable features.

One of the principal difficulties with molybdenum in high-speed steel is its tendency to volatilize at the high temperatures necessary in the working and hardening of the steel. Indeed, it is possible to detect high molybdenum steels under the hammer by the light yellow smoke arising, which is probably due to the oxide of molybdenum.

After prolonged or excessive heating, a well-defined zone on the outside of the bars or tools is entirely different from the interior in structure, and as a result, finished tools, such as drills and cutters,

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[2] C. H. Halcomb: U. S. Patent 722504 (March 10, 1903).

[3] J. A. Mathews: U. S. Patent 779171 (Jan. 3, 1905).

which cannot be given the grinding permissible with lathe tools are not satisfactory; this has greatly limited the use of molybdenum high-speed steels. Both vanadium and cobalt have been tried in an endeavor to overcome this difficulty. Recently it was stated that cobalt and vanadium are "stabilizers" for molybdenum, but the writer has seen no evidence to confirm these claims. On the other hand, molybdenum high-speed steel containing either or both of these elements has shown the defect in a marked degree. Some experiments now in progress promise more satisfactory results but it has not been determined whether our "stabilizer" in any way impairs the cutting qualities.

Cobalt-molybdenum-vanadium high-speed steel was made and abandoned in America before the beginning of the European war, for it was found inferior to the regular tungsten-vanadium steel products with or without cobalt. After reading recently that cobalt-molybdenum-vanadium high-speed steel was the latest foreign contribution to tool-steel metallurgy, some of the cobalt-molybdenum-vanadium material made in 1914, some ingots made along similar lines in 1919, and some of the European steel were used in exhaustive and carefully conducted tests made by the Halcomb Steel Co., in which the leading brands of American and foreign manufacture were used. The molybdenum products failed to give satisfactory results and were rated much below the standard tungsten high-speed steels on the market today.

For the modern developments in the use of molybdenum, we are greatly indebted to C. Harold Wills, of Marysville, Mich. Having become convinced that there was abundant ore in this country, he experimented with molybdenum in a great variety of combinations. Much has been published regarding the physical properties and suggested types of molybdenum-alloy steels but we would refer to the papers by Dr. Geo. W. Sargent,[4] J. D. Cutter,[5] and Chas. McKnight, Jr.,[6] the booklet entitled "Molybdenum Commercial Steels" by the Climax Molybdenum Co. and the booklet of the Crucible Steel Co. of America entitled "Almo Steels." While much of this material is propaganda, it is based on experiments made in our own laboratories and plants, in those of the Carbon Steel Co., United Alloy Steel Co. and by Messrs. Wills and Chandler, formerly with the Ford Motor Co. The paper by Doctor Sargent refers to the work of Guillet, Saladin, Swinden and Giolitti in reference to prior use and manufacture of chrome-molybdenum steels of somewhat similar types to those in which interest is now centered. Mr. Cutter's paper proposes the use

[4] Molybdenum as an Alloying Element in Structural Steels. Amer. Soc. Test. Mat. (1920).

[5] Suggested Method for Determining Comparative Efficiency of Certain Combinations of Alloy Steels. *Trans.* Amer. Soc. Steel Treat. (1920) **1**, 188.

[6] Molybdenum Steels. *Trans.* Amer. Soc. Steel Treat. (1921).

of a merit index for the comparison of different steels, and makes use of a formula in which the elastic limit, ultimate strength, elongation and reduction are all taken into consideration. A similar suggestion appears in the booklet "Almo Steels," in which the formula is limited to the tensile elastic limit and reduction of area.

In the mills, molybdenum steel has been found to work satisfactorily, being relatively as free from seams and similar defects as the older types of alloy steels; it is also freer from thick and tenacious scale than are the nickel and chrome-nickel types. It seems to flow readily, particularly in drop forgings, and can be worked over quite a wide range of temperature, say, from 2100° to 2500° F. (1150 to 1370° C.), though the higher temperature would not be recommended for steel containing above 0.25 to 0.30 per cent. carbon.

The steel seems to have a wide safe heat-treatment range, as measured by static tests. But it is not advisable to stress this point as it leads to carelessness in heat treatment. In addition, it has been found that static tests are somewhat misleading in this regard. While many steels of high quality can be forged or heat treated through a considerable range of temperature without apparent loss in static qualities, dynamic or shock tests seem to indicate that for every steel there is a temperature at which the maximum of static and dynamic qualities are obtained. Shock-test methods in this regard are of especial value in supplementing our knowledge of materials or even in detecting faulty heat treatments that static tests do not show. Molybdenum steels seem to machine more readily at a given Brinell hardness than do other steels. This would mean, of course, that parts that must be heat treated and machined afterwards could be utilized in a state showing higher physical properties than have been customarily obtainable. The physical property on which molybdenum seems to exert most effect is the reduction of area, which is usually considered a good measure of toughness.

Molybdenum, particularly in conjunction with chromium, seems to confer the property of deep hardening. This is to be expected from the observation that molybdenum steels resist the drawing temperature to quite an unusual degree. In other words, they require a higher drawing temperature to reduce the physical properties by the same amount that they would be reduced in similar steels without the presence of molybdenum. This indicates that molybdenum tends to keep the carbon in steel in the combined or martensitic form, and when in that condition to retard its passage to the sorbitic or troostitic state. Some years ago the writer sent to Prof. H. C. H. Carpenter,[7] then at the National Physical Laboratory of Great Britain, a chrome-molybdenum steel together

[7] H. C. H. Carpenter: Tempering and Cutting Tests of High-speed Steels. *Jnl.* Iron and Steel Inst. (No. 3, 1906) 71, 377.

with a variety of commercial high-speed steels for use in his investigations upon the drawing or softening of hardened high-speed steels. This particular steel contained but 4 per cent. of molybdenum, 3 per cent. of chromium, and about 0.47 per cent. carbon, yet it resisted the drawback temperature, as measured by Professor Carpenter's etching method, to a greater extent than any of the commercial tungsten high-speed steels used by him, whether of American or British manufacture.

It is possibly too early to make predictions, but the writer believes that molybdenum has established for itself a permanent place among the alloy steels found useful to the airplane, automobile and general engineering trades. It will not wholly displace any other type of steel, but the effect of improvements of this kind and new products has been rather to extend the field of usefulness than to eliminate products of previously demonstrated merit. The Bessemer and open-hearth processes, and the electric furnace have not displaced the original crucible cast steel business. The demand for steels made by each method has arisen with the process itself.

Not only does molybdenum below 1 per cent. give no trouble from volatilization, but it may be recovered from scrap when remelted in the open-hearth furnace to a large extent.

DISCUSSION

J. D. Cutter, New York, N. Y. (written discussion).—In his discussion of the characteristics of molybdenum structural steels, Doctor Mathews has covered all the outstanding qualities of these steels that have come under the observation of the writer, except perhaps the fact that such impact tests as have been made have been favorable. Doctor Mathews believes that these steels will not entirely replace any of the older alloy steels but that they will supplement and enlarge the sphere of usefulness of alloy steels in general. An illustration is the apparently marked adaptability of some molybdenum steels for sheet-metal parts, such as automobile frames, axle housings, rims, etc., a field in which the other alloy steels have not played a prominent part.

In this connection, the thought presents itself that perhaps the movement toward standardization of steel specifications should be carried a step farther and a single type of alloy steel be agreed upon as standard. Of course, such a standard would apply only for general purposes; there are many special cases where the fitness of a particular type of steel is unquestioned. Widely differing types of steel are now being used to meet almost identical conditions and the preferance of steel users for this or that type of alloy steel often is not based on fundamentals. The writer does not think that the time is ripe for such a move but offers this idea as a possible development of the future.

J. W. RICHARDS,* South Bethlehem, Pa.—A large maker of molybdenum steels said that he could put molybdenum into steel with less loss by using a molybdate salt than by using ferro-molybdenum. When we consider that in making ferro-molybdenum there is considerable loss in the electric furnace in which the ferro-molybdenum is made, the total loss of molybdenum should be much less when the oxidized compound is used directly, if it is efficiently reduced by the steel.

GEORGE WM. SARGENT,† Pittsburgh, Pa. (written discussion).—From the steel makers' point of view, as Doctor Mathews points out, the structural molybdenum steels are most desirable to manufacture, no unusual difficulties presenting themselves from the melting to the finished bar. The final yield is as great, even greater, than in the case of carbon steels; furthermore, there is no loss of molybdenum in the remelting of the scrap. The forging is attended with no exceptional features and the machining properties are excellent. The heat treatment is accomplished with greater ease, due to the wide range of temperature to which these steels may be heated before quenching, without deleteriously affecting the physical properties; and the effect of a greater variation in the drawing back, or annealing, temperature is less marked on the physical characteristics. As rolled by the producing mills, the tensile-test values are higher and more uniform even than carbon steels.

The Government tests of armor plate have shown that for resistance to the passage of the projectile, these chrome-molybdenum steels surpass chrome-nickel and other alloy steels. The tensile-test values from the transverse and longitudinal specimens are so nearly the same that the most satisfactory guns and other armament equipment requiring such similar characteristics have been made of these steels. Observation has shown that where the tensile-test values in the longitudinal and transverse test specimens are close to each other, the resistance to shock is usually good.

Automobile springs of chrome-molybdenum steels have demonstrated their superiority to the other alloy steels, not only in the static and laboratory tests, but also in service. Gears, connecting-rods, and crankshafts have proved most efficient when made from steel containing, in addition to molybdenum, either chrome or nickel, or both, though the chrome-molybdenum combination offers the greater ease of manufacture.

Doctor Mathews, referring to the effect of molybdenum, states that a tendency is indicated to keep the carbon in the combined or martensitic form, and when the carbon is in that condition, molybdenum retards its passage to the sorbitic or troostitic state. Whether this is the case,

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† President, Molybdenum Corpn. of America.

or whether the molybdenum retards the formation of ferrite or pearlite, preserving a martensitic or sorbitic state through a longer range of annealing temperature, is of no consequence, except from a scientific point of view. The result of the addition of molybdenum is a product that offers a solution to some of the difficult problems now confronting the users of steel.

The railroads with their heavy locomotives and larger freight cars have about reached the practical limit of section and carbon content in the steel rail; in fact, it would seem that these limits have been exceeded, if my deductions made from the reports of various investigators[8] are correct. The heavy rail sections are almost impossible to roll and finish at the uniform low temperature required to give a homogeneous fine grain structure with the high carbon steel necessarily used to give the required carrying capacity and wearing properties. Under service conditions, such rails develop interior defects that become fissures and eventually cause sudden breakage. Molybdenum, particularly in the presence of chromium, tends to give a product with a higher elastic limit. A lower carbon may, therefore, be employed, which would give a fine homogeneous uniform grain structure with the high finishing temperatures necessary to the manufacture of rails of large section. The following tensile-test values are of interest in this connection:

	Tensile Strength, Lb. per Sq. In.	Elastic Limit, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction of Area, Per Cent.
No. 1 chrome-molybdenum, as rolled, 1 in. round.....	140,000	105,000	15.0	32.0
No. 2 nickel-molybdenum, as rolled, 1 in. round.....	120,000	93,000	18.0	39.0

Analysis

	Carbon, Per Cent.	Chromium, Per Cent.	Nickel, Per Cent.	Molybdenum Per Cent.
No. 1.....	0.40	1.00	....	0.35
No. 2.....	0.40	....	1.50	0.40

Rails, therefore, of the carbon content in vogue when 80 lb. was a large section (0.50 to 0.60 per cent.) with 0.50 per cent. chromium and 0.25 per cent. molybdenum could be readily rolled and finished at the necessarily high temperature required for the 130-lb. section, producing a uniform fine grain and with an elastic limit in excess of the 0.80 per cent. carbon steel now in use. There would also be a corresponding increase of hardness. Such rails would have higher carrying capacity and offer less chance for the development of interior defects unde

[8] I refer particularly to the work of F. M. Waring and K. E. Hofammann: A. S. T. M. (1920), Pt. 2, 182; James E. Howard, A. S. T. M. (1920), Pt. 2, 44; and the investigations by the American Railway Association.

service conditions and greater resistance to wear. Such rails would be tougher and, before failure, would give previous surface indications. The first cost of rails of this composition would be higher than those made of straight carbon steel, but the results obtained from the chrome-molybdenum steel rails would make them even cheaper in the long run, not to mention the security obtained through their use.

The tensile-test value of ferrite and pearlite is low compared to that of semi-martensite or sorbite, the characteristic not only of molybdenum steels, but also of the tungsten and some of the higher chrome-nickel steels. Nickel and chrome-nickel steels have been used for rails, but the service tests were a disappointment for the reason that nickel, while it toughens, does not harden and it is necessary to keep the carbon content that of the normal straight carbon rail. The manufacturing difficulties, in addition, were such that sound rails were not always produced and the proposition, therefore, was not safe. This is but one case where molybdenum will extend the field of alloy steels.

Chrome-molybdenum steels are no more difficult to manufacture than low straight carbon steels, as has already been pointed out by Doctor Mathews and others.

On account of the greater tensile-test values obtainable from the chrome-molybdenum steels, as rolled, this material would seem to be especially suited to a certain type of bridges, notably the suspension of long span, whether constructed of eyebars or of cables. In such, weight is an important factor and the loading to a degree of approaching elastic limit is permissible. J. A. L. Waddell[9] states "An ideal structural material is an alloy steel to which the name chromol steel has been given, having the following composition: 0.25 per cent. carbon, 0.75 per cent. manganese, 0.75 per cent. chrome, and 0.75 per cent. molybdenum."

The addition of molybdenum to cast iron apparently increases the tensile-test values and resistance to shock, and at the same time it improves the machining qualities. In cast iron made with steel scrap addition, exceptional improvement is noted. Malleable castings thus made are exceptionally strong and tough.

[9] Comparative Value of Various Structural Steels for Bridge Building. *Genie Civil* (1920) **77**, 74.

An Experiment in One-piece Gun Construction

By P. W. Bridgman,* Cambridge, Mass.

(New York Meeting, February, 1920)

During the war, the Navy undertook the construction, under my direction, of an experimental gun embodying features designed to lessen the cost and time of production. These experiments were initiated after representations as to their desirability had been offered by myself, by the Naval Consulting Board, and by the National Research Council. The first drawings were made in June, 1917, and the experiment was completed in November, 1918.

For the sake of clearness it will pay to recapitulate briefly the fundamental idea of gun construction. It is well known that if a hollow cylinder is subjected to internal fluid pressure, the maximum stress occurs in the inside layers, the outer parts carrying much less than their due share of the stress. This inequality of stress is more pronounced the thicker the walls of the cylinder. If such a cylinder is pushed to the elastic limit, failure in elasticity will take place long before the outer layers have reached the limit of their capacity. Economical use of the material would demand, however, that all parts of the cylinder reach the limits of their capacity simultaneously. This may be brought about, at least in cylinders of not too great thickness, by producing in the inner layers an initial compression, and in the outer layers an initial tension. The effect of internal pressure is at first to relieve the compression of the inside layers, while increasing the tension of the outside layers. If the initial stresses are properly distributed, all parts of the cylinder will reach their elastic limits simultaneously, thus giving a cylinder of maximum strength for its weight.

In gun construction as hitherto practiced, this initial distribution of stress is produced either by winding the inner tube with wire, a common English practice, or by shrinking hoops over the inner tube, which has been the standard American practice. Either process is long and expensive, particularly with the larger guns, 12- or 14-in., which require

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seven or eight hoops at the breech, each of which must be machined inside and outside to one or two thousandths of an inch.

There is another possible method of producing the desired internal compression. If a heavy cylinder is stretched considerably beyond its elastic limit, the inner layers flow and the outer layers receive a permanent stretch. On release of pressure, the outer layers shrink back on the inner, producing an internal compression, and, of course, an equilibrating tension in the outside layers. If now pressure is reapplied, it will be found that the elastic limit has been raised to the previous maximum pressure. It is possible to raise the limit in this way to two or three times the value as calculated by the usual theories. This behavior of cylinders under high internal pressure was demonstrated experimentally, and has been continually used in the construction of apparatus for my high-pressure experiments at the Jefferson Physical Laboratory, since 1906. In these experiments I have accurately measured hydrostatic pressures as high as 300,000 lb. per sq. in. (21,090 kg. per sq. cm.), pressures which would have been unattainable except for this behavior of thick cylinders when stretched beyond the elastic limit.

The entire subject of the stress-strain relations in metal strained beyond the elastic limit is at present beyond the reach of theory (for instance, if a heavy cylinder is pushed to eventual rupture the crack starts at the outside instead of the inside surface), so that it is not possible to compute exactly the distribution of stress in a cylinder stretched as above, but approximate theory indicates a distribution of stress much like that of a built-up gun, and it is obvious at any rate that at the maximum pressure all parts of the gun must be pretty near the limit of their capacity. The application of this laboratory method to gun construction was obvious, and I had long had it in mind.[1] The procedure is to start with a single forging of approximately the dimensions of the finished gun, subject it to internal pressure (in one or more stages, depending on the external shape) high enough to stretch it permanently, and thus raise the elastic limit by producing a compression in the inside layers and a tension in the outside layers, and then to machine it to final dimensions. The pressures expected for the steels of ordinary gun construction would be of the order of 100,000 lb. per sq. in. (7030 kg. per sq. cm.). The firing pressure of a large gun is of the order of 30,000 lb. per sq. in. (2109 kg. per sq. cm.).

On examination, it appeared that the fundamental idea of raising the elastic limit by permanently stretching with an internal application of high pes sure was very old. The Austrians tried, in the eighteenth century, to accomplish it by forcing a steel expanding mandrel through the bore of the gun; there are English and French patents dating back to

[1] *Phil. Mag.* (July, 1912) **24**, 78.

the 1870's, and in this country there are the Emery patents between 1900 and 1904. There is also a theoretical paper by Turner.[2] None but the Austrians, however, had attempted to apply the idea in practise, and this fact was doubtless partly responsible for much of the skepticism as to the correctness of thp fundamental idea that was felt in various quarters. The probable reason why the idea had not been practically applied was the technical difficulty of making packings leak-proof at the pressures required. In my experiments, however, I had developed a technique by which pressure could be controlled up to the limit of the strength of the containing vessel.[3]

Just before the completion of the experiments, a report came that the French had succeeded, during the war, in reducing to successful practise the same idea by a method somewhat similar, and had in use, on the firing line, guns so constructed. The details of the method were not imparted, but it is probable that the stretching was performed by firing abnormally heavy powder charges in the gun.

From a purely scientific point of view, the proposed demonstration of the possibility of the process was superfluous, in view of the laboratory experiments, but from an engineering point of view it was possible that there might be unforeseen difficulties in getting homogeneous forgings of a large enough size, or that other obstructions might arise in passing from small- to large-scale work. In any event, an engineer finds it hard to resist a certain satisfaction in a large-scale demonstration which he does not entertain for an experiment of more academic dimensions.

The experiments were entirely successful, and the correctness of the fundamental ideas and the feasibility of construction were proved. The gun actually experimented with was a 3-in. (76 mm.), 23 caliber gun. A larger gun, either in bore or in length, would have been desirable, but the forging for this gun was the largest that the Washington Navy Yard could make, and the Navy Department was unwilling to interfere with production by asking any outside concern for a larger forging. After treatment and final machining, the gun was successfully tested for nine rounds at 21.8 tons per sq. in. (3065 kg. per sq. cm.). The usual test for a gun of this size is three rounds at a slightly less pressure. The pressure, in actual firing, is only 13 tons per sq. in. (1828 kg. per sq. cm.). With regard to cost and ease of manufacture, the following extract is taken from a report of the Commandant and Superintendent of the Naval Gun Factory, to the Bureau of Ordnance. "From this summary, it would seem that the actual saving of money would be inconsiderable for this type of gun, but it is undoubtedly certain that the saving of time, if quantity production should be attempted on this basis, would be enor-

[2] *Trans.* Cambridge Phil. Soc. (Sept., 1910).

[3] See Technique of High Pressure Experimenting. *Proc.* Amer. Acad. (Feb., 1914)

mous. Further, in the larger-type guns, it is thought that the simpler operations would involve the saving of a considerable amount of money as well as time."

Apart from proving the feasibility of gun construction by this method, the experiment has engineering interest concerning the means taken for controlling pressure of the required magnitude, and with regard to the elastic behavior of thick cylinders under high internal pressure.

The general scheme of the apparatus was as follows: the gun was plugged at both ends, one of the plugs being perforated to make connec-

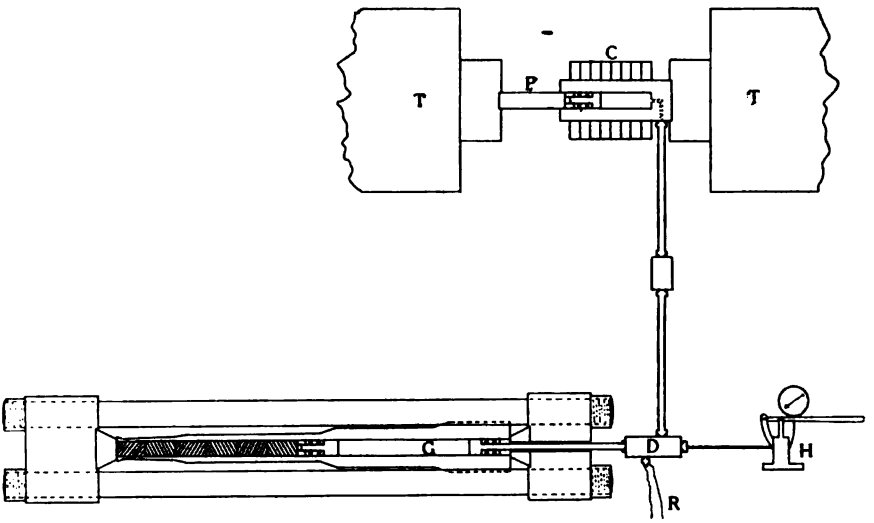


FIG. 1.—GENERAL ASSEMBLY VIEW. PRESSURE IS PRODUCED IN CYLINDER *C* BY PUSHING PISTON *P* WITH HEADS OF TESTING MACHINE *T*. PRESSURE IS TRANSMITTED THROUGH CONNECTING PIPES TO INTERIOR OF GUN *G*. WIRES *R* ARE CONNECTED TO MANGANIN RESISTANCE CAGE. INITIAL PRESSURE IS PRODUCED BY HAND PUMP *H*.

tion with a pipe leading to a cylinder and piston placed between the jaws of a hydraulic press. The interiors of gun and cylinder were filled with a suitable fluid, and any desired pressure was produced by operating the press.

No attempt was made to set up an apparatus capable of immediate commercial use; in this first experiment, the sole object was to show the correctness of the fundamental idea, and to that end the experimental set-up was designed so as to be simple and inexpensive using, so far as feasible, resources already available. A general assembly view of the apparatus is shown in Fig. 1. For the press with which the piston was driven into the cylinder, the 2,000,000-lb. (907,200-kg.) Emery testing machine of the Bureau of Standards was used, the machine being set up for tests in compression. The use of the Emery machine made it necessary to perform the actual stretching of the gun at the Bureau of Standards. I thank Doctor Stratton, Director of the Bureau, for the use

of the press and the courteous way in which the resources of the Bureau were placed at my disposal.

In Fig. 1 the testing machine is indicated by the two press heads; in use, the right-hand head was stationary, the left-hand head moving toward it, driving the piston into the cylinder. The interior diameter of the cylinder was 3 in. (76.2 mm.). The area of a circle of this diameter is 7.07 sq. in. (45.6 sq. cm.) so that the estimated pressure of 100,000 lb. per sq. in. (7030 kg. per sq. cm.) in the gun would require a thrust of 707,000 lb. (320,685 kg.), exclusive of friction, on the piston. The necessity of a large press is therefore evident. The cylinder was made in two parts. The central part was 22 in. long and 8 in. in diameter (56 by 20 cm.), of Cr-Ni steel having an ultimate strength of 275,000 lb. per sq. in. (19,332 kg. per sq. cm.) and an elastic limit of 240,000 lb. (16,872 kg. per sq. cm.) with an elongation of 5 per cent. Over this central core were shrunk eight rings of the same steel, 15 in. (38 cm.) outside diameter, and 2 in. (5 cm.) thick. It was necessary to build up the cylinder in this way in order that all the metal parts might be comparatively thin, so that the effect of heat treatment might extend throughout the mass of the metal. The piston was of glass-hard tool steel, 13 in. long and 2.995 in. diameter (33 by 7.607 cm.). I have found in all my work that pistons which are to take a pure thrust are much better left glass-hard.

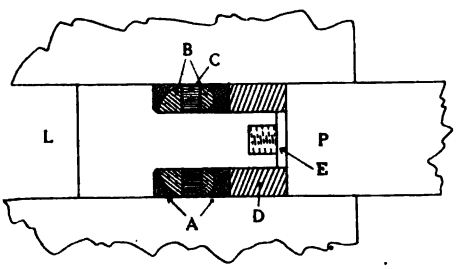


FIG. 2.—DETAILS OF PACKING PLUG OF CYLINDER. PISTON *P* PUSHES PLUG TOWARD LIQUID AT *L*. *A* IS SOFT STEEL, *B* SOLDER, *C* SOFT RUBBER, *D* HARDENED STEEL. *E* IS UNSUPPORTED AREA BACK OF THE PLUG.

The packing plug, driven by the piston into the cylinder, is shown in Fig. 2. Its principle is such that the pressure in the packing is automatically maintained any desired percentage higher than the pressure in the liquid, making leakage impossible. It has been fully described in the paper on technique already cited. The plug consists essentially of a plunger with a stem, the packing, which is ordinary soft rubber, being placed around the stem. The rear end of the stem slides in a hardened steel ring of such thickness that this end of the stem is left without longitudinal support. The principle of operation is as follows. Since the plunger is in equilibrium at any stated pressure, the total force exerted by the liquid in one direction on the plunger head must be balanced by the total force in the other direction exerted by the annular shaped pack-

ing. But the area on which the liquid acts is greater than that on which the packing acts, so that the intensity of pressure in the packing is greater than that in the liquid. In particular, if the diameter of the stem is one-half that of the plunger head, the area of the ring is 75 per cent. that of the head, so that the pressure in the packing is 33 per cent. greater than that in the liquid. This principle of an unsupported area (in this case the free end of the stem shown at *E*) is capable of the most varied modification, and by the use of it any problem in high-pressure packing may be solved. In Fig. 2 the various auxiliary packing rings of steel or solder keep the rubber in place.

The connecting pipe leading from the cylinder was 1¼ in. (3.18 cm.) outside diameter, and ⅛ in. (3.2 mm.) inside diameter. It was made of the same Cr-Ni steel as the cylinder, drilled from the solid rod, and turned to final dimensions, on centers, after drilling. Because of the difficulty of drilling longer holes of a diameter smaller than ⅛ in., the pipe was made in 30-in. lengths. Two lengths were necessary to lead from the cylinder to the axis of the gun, and these were connected by a right- and left-handed coupling, of obvious design. The packing at the ends of the pipe used the same principle of unsupported areas as just described, but the details were different, the packing material in this case being soft-steel rings. The details of this pipe packing are shown in Fig. 10, page 639, of the paper on technique.[4]

The gun is shown in position in a heavy steel yoke, by which the plugs at both ends were prevented from blowing out. The two ends of this yoke were forgings of mild steel, 21 in. (53 cm.) square and 12 in. (30 cm.) thick. There were four tie rods of mild steel, 5 in. (12.7 cm.) in diameter and 9½ ft. (2.9 m.) long. The right-hand head of the yoke was pierced centrally to allow entrance of the connecting pipe to the breech of the gun. This pipe made connection at one end to a right-angled coupling piece *D*, to which the pipe was brought from the cylinder, and at one end connected with the interior of the gun. The packing on the gun end of this pipe was essentially like that shown for the cylinder. The stem of the plunger was here replaced by the straight shank of the connecting pipe, and the head of the plunger by a head turned on the pipe. The packing plug at the muzzle end of the gun was essentially a duplicate of that for the cylinder, except that the conical steel parts were made longer and more tapering to take up the stretch during application of pressure. Some means of providing for a follow-up by the packing during stretch is essential, and the method shown was entirely successful.

The right-angled coupling *D*, besides connecting the pipes from cylinder and gun, contained two other essential parts of the apparatus. At the right-hand end of this coupling, connection was made through a check valve to a hand pump, the function of which was to produce an

[4] *Proc.* Amer. Acad. (Feb., 1914).

initial pressure throughout the apparatus before the press started to drive the piston into the cylinder. Without this precaution, so much of the stroke of the piston would have been wasted in squeezing out air bubbles and in giving the initial rather large compression to the transmitting liquid, that it would not have been possible to reach the desired maximum pressure in the one stroke to which the apparatus was limited. The hand pump, which was one I had specially constructed for my experimental work, gave an initial pressure of 20,000 lb. per sq. in. (1406 kg. per sq. cm.).

The check valve was of obvious design, consisting of a carefully ground, hardened steel cone of about 90° angle, held tightly against its seat by a very heavy spring. It probably was not absolutely leak tight, but any leakage was not fast enough to be perceptible with apparatus of this scale, although it might be more troublesome with smaller apparatus.

Beside the connection to the low-pressure pump, the right-angled coupling contained the device for measuring pressure. It would have been easier if the pressure could have been computed from the area of the piston and the total thrust on the jaws of the testing machine, but the friction was so great as to make this impossible. For instance, at an actual pressure in the gun of 80,000 lb. per sq. in., the calculated pressure, making no allowance for friction, was 110,000 lb., showing a loss by friction of 30,000 lb. per sq. in. (27.3 per cent. of the calculated) or 210,000 lb. total thrust in the machine. It was therefore, necessary to measure the pressure in the gun directly. For this measurement, no ordinary type of gage, such as a Bourdon, is suitable, because of insufficient strength and too great elastic hysteresis. In my laboratory experiments, I had successfully used a manganin resistance gage, and this was used successfully here. This method of measuring pressures utilizes the change in resistance of a metal under pressure. Manganin is particularly suitable because of the linearity of the relationship, and the negligible effects of temperature changes. The magnitude of the variation in resistance is about 1.6 per cent. for 100,000 lb. per sq. in. (7030 kg. per sq. cm.). With modern commercial apparatus, a change of this magnitude may be easily measured with the required accuracy. Details of the method may be found on page 640 of the paper on technique,[5] and also in another paper.[6] For the actual details of the method of measuring resistance employed in connection with this gage, and for the apparatus, I am indebted to E. L. Purrington, of the Bureau of Standards.

The approximate dimensions of the gun, of a type now superseded, are shown in Fig. 3. This gun is especially simple in that the outside,

[5] *Loc. cit.*

[6] The Measurement of Hydrostatic Pressures up to 20,000 kg. per Square Centimeter. *Proc.* Amer. Acad. (Dec., 1911) **47**.

over the region in which the greatest powder pressure is exerted, consists of two cylinders of outside diameters 7.5 and 5.3 in. (19 and 13.5 cm.), respectively. The extreme muzzle, which is conical, need not be considered, because when the projectile has reached this part of the gun, the powder pressure has dropped so low as to make unnecessary any treatment of this portion.

It was necessary to apply the pressure in two stages, first to the breech alone, and second to the muzzle and breech, because a pressure high enough to stretch the breech sufficiently would have stretched too much and probably ruptured the muzzle. The two-stage application of pressure was accomplished as follows. The packing toward the muzzle was first placed at the region of decrease of outside diameter from 7.5 to 5.3 in., and held in this position by hardened steel blocks filling up the rest of the bore of the gun to the extreme muzzle. Thrust was transmitted through these blocks to the left-hand head of the yoke. The region open to pressure was thus restricted to the breech end of the gun, which thereupon stretched

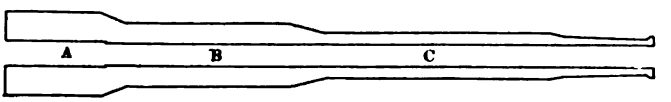


FIG. 3.—SCALE DRAWING OF THE GUN BEFORE TREATMENT. THE OVER-ALL LENGTH IS 77 IN. (195.6 CM.) INSIDE DIAMETER AT *A*, 2.7 IN. (6.86 CM.); INSIDE DIAMETER AT *B* 2.6 IN. (6.6 CM.), AND OUTSIDE DIAMETER 7.5 IN. (19 CM.); INSIDE DIAMETER AT *C* 2.6 IN. AND OUTSIDE DIAMETER 5.3 IN. (13.5 CM.).

to the required amount. Pressure was then released, the blocks retaining the left-hand packing plug were removed, and pressure was reapplied. The left-hand packing, now unsupported, was driven to the left by the pressure until stopped by the left-hand head of the yoke, leaving the breech and the muzzle accessible to pressure, which was then reapplied with sufficient force to stretch the muzzle. This pressure being less than that previously applied to the breech, because of the smaller dimensions of the muzzle, no additional permanent effect was produced at the breech.

The packing evidently had to be of such design that it would allow considerable stretch of the inside without leak, and could be moved from one position to the other without too great force and without leakage; it must also be used a second time in the new position, again without leak. The packing here illustrated satisfactorily answered these requirements. The maximum pressure required to overcome its friction was 35,000 lb. per sq. in. (2460 kg. per sq. cm.) and after the sticking point was passed a pressure of 2000 lb. per sq. in. moved it easily.

The details of the actual stretching were as follows. Four applications of pressure in all were made. The first of these, to the breech alone, was made on June 20, 1918, with unsuccessful results. Through

some misunderstanding, the kerosene specified as the filling fluid was not provided, and it was necessary to use a substitute having untried properties. The danger was that the oil might freeze under the high pressure, and thus refuse to transmit the pressure. This was actually what happened. The total thrust applied by the Emery machine was 1,300,000 lb., corresponding to 180,000 lb. per sq. in. in the cylinder, making no allowance for friction; of this pressure, only 95,000 lb. per sq. in. was recorded by the manganin gage, and, judging by the elastic behavior, only 78,000 lb. reached the inside of the gun. Under the extreme thrust, the pipe ruptured at the end nearest the cylinder, the cylinder itself was somewhat scored on the inside, and the piston was slightly upset. Repairs were made, and the next application of pressure, this time with the proper transmitting medium, was made to the breech on July 26, 1918. On the morning of July 27 the packing was driven back to the muzzle, and in the afternoon pressure was applied to both breech and muzzle, stretching the latter. On the morning of July 29, pressure was reapplied to the entire gun as a check on the raising of the elastic limit. The gun was then dismantled and sent to the Naval gun factory for finishing. It was turned, inside and out, rifled, the breech mechanism put in place, and the final firing tests, already mentioned, were made late in November, 1918.

The manner of yield during application of pressure now remains to be described as this offers some interesting features relating to the strength of materials. Measurements to 0.0001-in. (0.0025 mm.) were made with a micrometer on the outside diameter of the gun at a number of points, during and after each application of pressure, and on the inside diameter before and after the complete treatment. Interest in the results themselves would have warranted more careful measurements, but I did not feel justified in making a more elaborate study than was demanded by the needs of the moment.

In Fig. 4 is shown the relation between external diameter (mean of three readings at the center of the breech section) and pressure, during the initial application of pressure to the breech on June 20. Beyond 55,000 lb. per sq. in. the observed curve showed a break, due to the incipient freezing of the transmitting oil, so that the recorded pressures corresponding to the measured diameters were too high. It is possible, however, to estimate, from the behavior on the next application of pressure, that a maximum pressure of 78,000 lb. per sq. in. (5483 kg. per sq. cm.) was reached on the first application. The probable course of the true curve between 55,000 and 78,000 is shown dotted in the figure. A total set of 0.0037 in. (0.094 mm.) on the outside diameter was produced by the first application. The feature of particular interest in Fig. 4 is that there is no evidence of an elastic limit anywhere, on increasing pressure, but the stress-strain curve from the beginning shows pronounced curvature.

This is not surprising in this material, which could not have been left by the forging in a state of complete ease.

The linear relation to be expected between stress and strain in a cylinder of these dimensions may be computed from the theory of elasticity

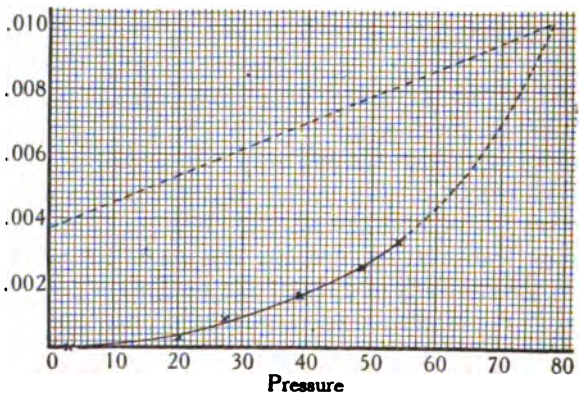


FIG. 4.—FIRST APPLICATION OF PRESSURE TO THE BREECH. THE INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST THE INTERNAL PRESSURE (ABSCISSA) IN THOUSANDS OF POUNDS PER SQUARE INCH.

as given in any textbook. (See, for example, Love's "Elasticity," p. 141.) We have for the radial displacement U,

$$U = Ar + \frac{B}{r}, \qquad A = \frac{pr_1^2}{2(\lambda+\mu)(r_0^2 - r_1^2)} - \frac{\lambda e}{2(\lambda+\mu)},$$

$$B = \frac{pr_0^2 r_1^2}{2\mu(r_0^2 - r_1^2)}.$$

where p is the internal pressure, r_1 internal and r_0 external radius, λ and μ the two elastic constants. The longitudinal strain of the cylinder e is connected with the longitudinal fiber stress Z_z by the relation

$$Z_z = \frac{\lambda}{\lambda+\mu} \times \frac{pr_1^2}{r_0^2 - r_1^2} + e\frac{(3\lambda+2\mu)\mu}{\lambda+\mu}.$$

In a cylinder mounted, as this was, so that the thrust on the end plugs was taken by an outside frame, we have, neglecting friction, $Z_z = 0$.

Taking as average values for the elastic constants of steel

$$\left.\begin{aligned}\mu &= 8.2 \times 10^{11} \\ \lambda &= 1.12 \times 10^{12}\end{aligned}\right\} \text{Abs. C. G. S. units,}$$

we find that $e = -2.59 \times 10^{-4}$ for 100,000 lb. per sq. in. That is, the gun shortens under internal pressure applied as above. With this value for e, we find

$$\left.\begin{aligned}A &= 3.18 \times 10^{-4} \\ B &= 3.31 \times 10^{-3}\end{aligned}\right\} \text{ for 100,000 lb. per sq. in.}$$

Substituting now the numerical values of 7.5 in. for the outside diameter, and 2.6 in. for the inside diameter (the gun was made 0.4 in. small on

the inside to allow for stretch) we find $U = 3.4 \times 10^{-3}$ for 100,000 lb. per sq. in. That is, the outside diameter should increase 0.0068 in. (0.173 mm.) under 100,000 lb. per sq. in. (7030 kg. per sq. cm.) internal pressure. The slope of the initial part of the curve in Fig. 4 is much less than this, while that of the latter part during stretch is, of course, much greater. The recovery after release of pressure was, however, at the rate of 0.0080 in. (0.203 mm.) per 100,000 lb. That is, the first applica-

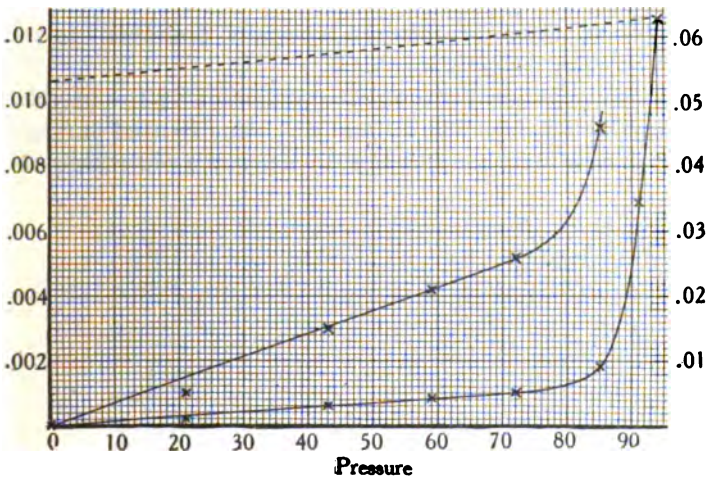


FIG. 5.—SECOND APPLICATION OF PRESSURE TO BREECH. INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST INSIDE PRESSURE (ABSCISSA) IN THOUSANDS OF POUNDS PER SQUARE INCH. RESULTS ARE SHOWN ON TWO SCALES; LEFT-HAND SCALE APPLIES TO UPPER CURVE, WHICH SHOWS STRAIN BEFORE PRONOUNCED FLOW HAS BEGUN, AND RIGHT-HAND SCALE APPLIES TO LOWER CURVE, WHICH SHOWS STRAIN DURING BOTH STAGES OF ELASTIC YIELD AND OF FLOW.

tion of pressure, in spite of some permanent set, has left the metal with effective elastic constants approaching those of a state of ease.

The elastic limit to be expected on the maximum stress theory can be easily computed. At the inner surface we have

$$\Theta_\theta = \frac{r_0^2 + r_1^2}{r_0^2 - r_1^2} p,$$

where Θ_θ is the circumferential fiber stress. The elastic limit of this steel was about 60,000 lb. per sq. in. (4218 kg. per sq. cm.). Substituting this value for Θ_θ gives 46,500 lb. per sq. in. (3269 kg. per sq. cm.) as the expected elastic limit of a cylinder initially without internal stress and in a state of complete ease.

The results of the second application of pressure to the breech, on July 26, are shown in Fig. 5. Pressure was pushed to a maximum of 94,000 lb. per sq. in. (6609 kg. per sq. cm.) producing an additional permanent set of 0.053 in. (1.35 mm.) on the outside. This additional set took

place almost entirely above 85,000 lb. In the diagram, the results are plotted on two scales; on a large scale showing the results to 85,000 lb., and on a scale five times smaller to show the flow and set. It is evident that the initial stress-strain relation is much more nearly linear on the second than on the first application of pressure. The best straight line through the points up to 73,000 lb. has a slope of 0.0072 in. per 100,000 lb., which is close to the theoretical elastic rate. The rate of recovery after release of pressure was at the rate of 0.0103 in. per 100,000 lb., which is considerably more than the elastic rate. This is to be explained by hysteresis effects, which are always especially prominent in metal which has been recently severely strained.

The stress-strain relations on the next application to the breech, on July 27, are shown in Fig. 6. The muzzle was being treated during this application, so that it was not possible to reach the old maximum of

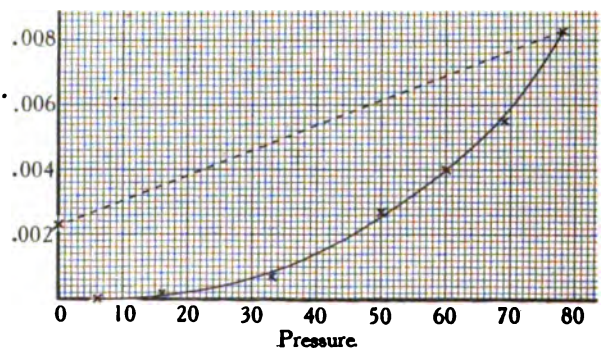


FIG. 6.—THIRD APPLICATION OF PRESSURE TO THE BREECH. THE INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST THE INTERNAL PRESSURE IN THOUSANDS OF POUNDS PER SQUARE INCH.

94,000 lb., 78,000 lb. (5483 kg. per sq. cm.) being all that was required to give the muzzle the desired stretch. The breech received an additional stretch of 0.0023 in. (0.058 mm.) during this third application. The stress-strain relation shows just as pronounced curvature as it did on the first application. This is evidently an effect of the previous severe straining and considerable flow produced by 94,000 lb.; the interior of the metal had been thrown into a state of disturbed internal equilibrium. A state of ease may be recovered after such treatment by prolonged resting; it is also known that the speed of recovery is greatly increased by moderate heating. The elastic recovery on release of pressure after the third application was at the rate of 0.0076 in. per 100,000 lb., again approaching the theoretical rate.

The results of the fourth application to the breech, on July 29, are shown in Fig. 7. One observed point was discarded because it was so far off the curve that it was evident that a blunder had been made in reading.

Two readings were made with decreasing pressure, an observation not previously made. The relation between stress and strain is now much more nearly linear. The whole cycle of operations forms an open hysteresis loop, such as is quite characteristic of the behavior of heavy masses of metal strained far beyond the elastic limit. I have elsewhere[7] shown examples of such loops obtained under other conditions. The permanent stretch, after this fourth application, was only 0.0007 in. (0.018 mm.). In such cases as the present, the conventional terminology breaks down, but it is to be questioned whether such slight permanent alterations of dimensions as have been shown after the first, third, and fourth applications of pressure are correctly characterized as set, in the understood sense of the word, but are not rather to be recognized as a result of the internal accommodation that has evidently taken place, as shown by the character of the stress-strain curve under increasing stress.

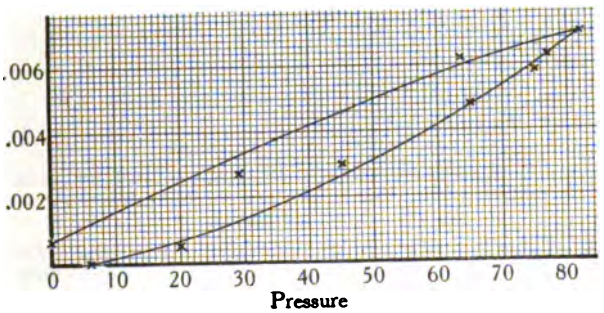


FIG. 7.—FOURTH APPLICATION OF PRESSURE TO THE BREECH. THE INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST THE INTERNAL PRESSURE IN THOUSANDS OF POUNDS PER SQUARE INCH.

The result of the initial application of pressure to the muzzle is shown in Fig. 8. As in Fig. 5, results are plotted on two scales, a larger scale for the points before pronounced set occurred, and a scale five times smaller showing set. Just as in the case of the breech, the stress-strain relation on the initial application was not even approximately linear, but the curve started with pronounced curvature, passing into the region of flow without abrupt change of direction.

The diameters of the muzzle were 5.3 in. (13.5 cm.) outside, and 2.6 in. (6.6 cm.) inside. Applying computations similar to those for the breech, we find that the longitudinal strain is a shortening of 6.0×10^{-4} for 100,000 lb. per sq. in., that the theoretical elastic increase of diameter is 0.0111 in. (0.28 mm.) per 100,000 lb., and that the theoretical elastic limit, on the maximum stress basis, is 37,000 lb. (2600 kg. per sq. cm.). The maximum stress applied was 78,000 lb. The rate of recovery after release of pressure was 0.0119 in. (0.3 mm.) per 100,000 lb. per sq. in., much more nearly the theoretical rate than was shown by the thicker

[7] *Phys. Rev.* (1912) **34**, 11.

breech, in spite of the fact that the set was relatively and absolutely greater, 0.0767 in. (1.95 mm.) against 0.0530 in. (1.35 mm.).

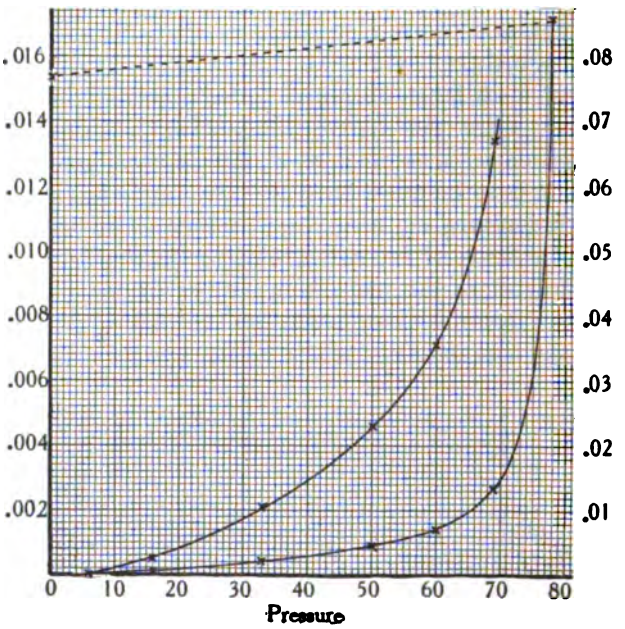


FIG. 8.—FIRST APPLICATION OF PRESSURE TO MUZZLE. INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST INTERNAL PRESSURE IN THOUSANDS OF POUNDS PER SQUARE INCH. RESULTS ARE SHOWN ON TWO SCALES; LEFT-HAND SCALE APPLIES TO UPPER CURVE, WHICH SHOWS STRAIN BEFORE PRONOUNCED FLOW HAS BEGUN, AND RIGHT-HAND SCALE APPLIES TO LOWER, WHICH SHOWS STRAIN DURING STAGES BOTH OF ELASTIC YIELD AND OF FLOW.

The result of the second application of pressure to the muzzle is shown in Fig. 9. The initial relation between stress and strain is linear within the limits of error of measurement, with a slope of 0.0106 in. (0.27 mm.) per 100,000 lb. The agreement with the calculated value is probably within the limits of error of the values assumed for the elastic constants. This linear relation is in striking contrast with the curvature shown in Fig. 5, taken under corresponding conditions at the breech. This agrees with all my previous experience that, after flow, equilibrium is attained much more rapidly in small than in large masses of metal, and that accommodation effects are always much less prominent. Briefly, the explanation of this is that in the smaller mass of metal there is less room to set up those internal stresses and inhomogeneities, the releasing of which causes the accommodation effects.

The previous pressure maximum of 78,000 lb. was slightly exceeded on the second application, pressure being pushed to 82,000 lb. The slight additional set of 0.0039 in. (0.1 mm.) on the second application was almost entirely produced by this excess pressure. On release of pressure, there were pronounced hysteresis effects, doubtless the result of the

slight additional flow produced by the excess 4000 lb. The total recovery on release was at the same average rate as the linear rate on application of pressure, namely 0.106 in. (2.7 mm.) per 100,000 lb. per sq. in.

After completion of the stretching, the bore was measured at the Navy

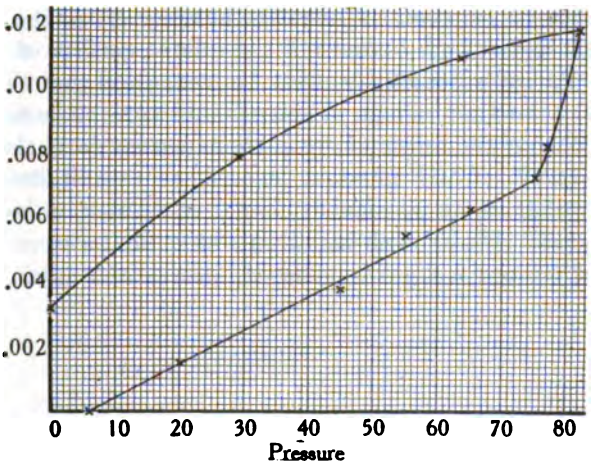


FIG. 9.—SECOND APPLICATION OF PRESSURE TO THE MUZZLE. THE INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST THE INTERNAL PRESSURE IN THOUSANDS OF POUNDS PER SQUARE INCH.

Yard. Fig. 10 shows the internal permanent stretch at various points of the bore. The minimum at 33 in. corresponds to the transition from breech to muzzle. With the experience gained from this first trial it would evidently be possible to improve the position of the packing plugs so that the

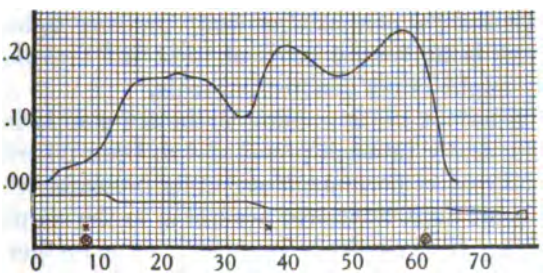


FIG. 10.—TOTAL INTERNAL STRETCH AFTER TREATMENT, IN INCHES (ORDINATE) AS FUNCTION OF POSITION, IN INCHES, ON AXIS OF GUN (ABSCISSA). CROSSES SHOW POSITION OF PACKING DURING APPLICATIONS OF PRESSURE TO BREECH ALONE, AND CROSSES IN CIRCLES POSITION OF PACKING DURING APPLICATION OF PRESSURE TO BOTH BREECH AND MUZZLE.

stretch of breech and muzzle would join each other continuously. The minimum at 48 in., on the other hand, must have been an intrinsic irregularity due to a local hardness in the forging. However, the stretch at all points of the bore was sufficiently great so that local irregularities had no bad effect, as shown by the final firing tests.

From a comparison of the final outside and inside dimensions, some idea can be gained as to whether there was any permanent change of density of the metal. At the center of the breech section, the computed metal added to the outside of the cylinder agreed with that taken from the inside to within 0.7 per cent. but at the muzzle the agreement was only within 14 per cent. However, the accuracy of the computation at the muzzle is not high because of the inhomogeneity of the metal, and, in particular, the possibility must be recognized that the figure did not remain circular; not enough measurements were made to be sure of this point. Within the limits of error, there was no great change of density. It is a result of my previous experience that hydrostatic pressure, as such, produces no permanent change of density, unless the metal has actual pores. Under such conditions of strain as were employed here, the density shows a slight tendency to decrease, if anything.

Summary

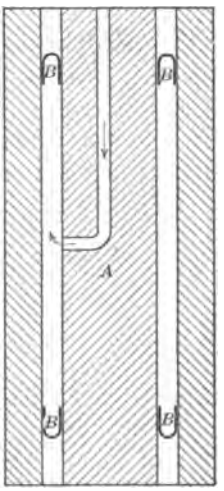
1. With regard to gun fabrication, it has been demonstrated by actual construction and firing tests that it is possible to make a gun from a single forging, producing the required distribution of internal stresses by a preliminary application of hydrostatic pressure so high as to strain the material considerably beyond its yield point. The great simplicity of construction by this method leads to the expectation of important economies of time and money if quantity production should be attempted.

2. The technique of controlling the pressures required, which are of the order of 100,000 lb. per sq. in. (7030 kg. per sq. cm.), has been described as applied to the experimental gun. The essence of the technique is a packing which automatically becomes tighter at higher pressures. There is no reason to think that the technique should not be successfully applied on a commercial scale.

3. The behavior of the hollow cylinders composing the gun, when stretched by heavy internal pressure, has been described. Such cylinders flow and receive permanent set under pressures which may be about twice the elastic limit computed according to the simple theories. After once stretching, the cylinder receives little or no further permanent set up to the previous pressure maximum. Within this range of pressure, the cylinder behaves in a manner approaching that of perfect elasticity, but with very marked disturbances, of which hysteresis and accommodation effects are the most prominent. These disturbances tend to disappear with time. The approach to perfectly elastic behavior is much closer for thin than for thick cylinders. A valid theory of the stress-strain relations under such conditions is much to be desired, but has not yet been formulated.

DISCUSSION

FEDERICO GIOLITTI, Rivoli, Italy.—In the last year of the war we turned out many guns in one piece by applying the principle outlined. At first, we had some difficulty in making large guns, because of the necessity of making a big press for keeping the pressure in the gun; we solved that difficulty by the device here shown. The same principle was applied in France, in the last two years, for the cold relining of guns. For applying the pressure in the gun, we used a device similar to the one shown in the accompanying illustration. A cylinder *A*, a little smaller than the inside diameter of the tube was inserted and the space between the cylinder and the tube was closed by U-shaped leather bands, *B*; the rings were able to stand very high pressures without displacing, and were used in the big guns to keep the pressure inside of the tubes. In that way we succeeded in expanding the metal of 10-in. guns manufactured in the regular way, and many of our guns were made by this process. It is unnecessary to put on any particular press to keep the pressure inside of the gun.



HENRY D. HIBBARD, Plainfield, N. J.—About 20 or 30 years ago, the Bofors Works, Sweden, made guns which were cast in one piece and simply annealed; tests showed them to be practically unbreakable. According to the reports published at that time, they were tested by increasing charges until, finally, the gun was entirely filled with shot, the last one projecting from the muzzle. They put that up against a great block of iron and fired, with the result that the gun went pirouetting off through the trees and became the projectile while the shot stayed behind. It seemed as if the strength was all that could be desired, yet for some reason or other the manufacture of the guns was discontinued. A gun of that kind treated as described by Mr. Bridgman might prove to be the ideal gun and be produced even more cheaply than the forged gun.

P. W. BRIDGMAN.—I never heard of that gun and so can say nothing about it; but I would like to call attention to the fact that the most difficult problem is not to produce a gun of sufficient strength, but to produce a gun that will not stretch. Any gun can have its elastic limit raised during firing by an automatic application of this process that I have applied, the exploding charge of powder supplying the pressure, but you will have to stretch the gun to do it. The important problem is to raise the elastic limit rather than the ultimate strength.

Manufacture of Semisteel for Shells

By Frank E. Hall,* M. S., Buffalo, N. Y.

(New York Meeting, February, 1920)

The needs of the World War showed the necessity of a metal stronger than cast iron which would supplement the supply of steel. So patriotic metallurgists were spurred to new efforts to improve the status of that half-breed of the metal world that had been, more or less erroneously, christened semisteel. As a result, it was developed that for certain purposes semisteel was superior to steel in the manufacture of shells.

Steel, because of its greater strength and toughness, is able to carry a greater charge of explosive, weight for weight; consequently, a steel shell can be expected to cause greater destruction when used against fortifications or other inanimate objects, while semisteel, because of its comparative brittleness and its resulting greater fragmentation, is capable of inflicting more serious loss of life when used against opposing forces of men. Therefore, each has its proper place in the economy of war.

For the present purpose, steel may be defined as a comparatively pure iron whose physical nature is modified by small amounts of carbon, silicon, sulfur, phosphorus, manganese, and possibly other rarer elements; while cast iron generally is limited to approximately 93 per cent. of iron, the remainder consisting of larger percentages of carbon, silicon, sulfur, phosphorus, and manganese. Semisteel may be defined as cast iron in which the carbon and silicon have been reduced to as low a point as is consistent with maintaining the nature of gray iron, and in which the remaining elements are adjusted so as to give the greatest strength.

The fact that the addition of steel scrap, in varying percentages, is the means used to reduce the carbon, together with the fact that a considerable increase in strength results, is probably the explanation of the origin of the name semisteel. That ordinary grades of steel show from three to four times the tensile strength of cast iron is due to the fact that the crystals, or grains, of cast iron are interspersed with flakes of

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graphitic carbon, which break up the continuity of the mass and form surfaces of cleavage, which weaken the whole structure. Ordinarily about 3 per cent. of graphitic carbon is present in cast iron, but as the specific gravity of graphite is 2.15 and of cast iron 7.20, the space occupied by the graphite is upward of 10 per cent.; so when it is considered that the graphite is present in flakes, or plates, and not in grains, the reduction in strength is easily understood. The production of semisteel involves a reduction of graphitic carbon to approximately 2.40 per cent. In addition, the reduced silicon content and other factors entering into the situation tend to change the flakes of graphite into finer particles of more compact shape, rendering the structure more homogeneous and, consequently, stronger. It is easily possible to double the strength of ordinary cast iron by the addition of steel scrap and the proper manipulation of the controlling constituents.

Chemical Requirements of Semisteel

A number of features are of pressing importance in securing consistent results. Foremost among them are the careful control of the chemical composition of the metal and extreme care in maintaining uniformly the proper melting conditions as well as the conditions surrounding the pouring and subsequent heat treatment of the castings. As increased strength is the main object sought, the carbon and silicon must be reduced. The extent to which this reduction may be carried is limited by the size of the casting, the material of which the mold consists, the subsequent heat treatment, and, to some extent, by the percentage of sulfur and manganese contained. The lower the total carbon, the greater is the tendency of the carbon to remain in the combined state for any given silicon content; so in order to safeguard the castings from "chilling white" it is necessary to increase silicon as the total carbon decreases. A generally accepted rule is that for a shell of 155 mm. in diameter or larger, the total carbon plus the silicon should be maintained at approximately 4.40 per cent., although it will be seen from the analyses in Table 1 that excellent results have been secured with a total considerably below this figure.

The total carbon is more difficult to control than is the silicon, for in the cupola, carbon is absorbed from the fuel in varying amounts, depending on the conditions surrounding the melting. As a result the total carbon is always greater than the calculated amount, and it is not always possible to forecast accurately the reduction that will result from the use of a given amount of steel scrap. The silicon, on the other hand, loses more through oxidation than is the case in melting ordinary gray iron; and while a better control of the silicon content is possible than of the carbon, the variations are such that accurate and

rapid laboratory methods are imperative in order that as close control of the composition as possible may be maintained.

In addition to the requirement for high tensile strength, the manufacture of shells demands a certain degree of toughness, or freedom from excessive brittleness, to insure against breaking in the gun. This feature involves carrying a low phosphorus content, in addition to the precaution against allowing the total of the carbon and silicon to become so low that brittleness will result. In order to meet the present requirements in this respect, a phosphorus content not to exceed 0.120 per cent. is desirable.

The effect of manganese is practically the same as in the case of ordinary gray iron and, as in the case of other low-silicon castings, is preferably carried from 0.75 to 1.00 per cent.

Sulfur, never a desirable constituent, tends to increase abnormally in semisteel, due to a number of conditions. Chief among these is the ready absorption of this element by the steel scrap, which necessarily consists of moderate-sized pieces. As these become red hot before the larger pieces of pig iron and require greater heat to melt, they remain longer in contact with the sulfurous gases from the fuel. As the latter is required in greater amount in order to insure the proper melting of the steel scrap, it naturally furnishes more sulfur. The rigid requirements of the manufacture of semisteel shells involve a larger percentage of remelt than in ordinary practice, which also tends to a higher sulfur content, so that special care is needed in the selection of materials and attention to the details of the process to insure as low a percentage of sulfur as possible.

In Table 1 are given a number of selected analyses with the results of the accompanying tensile and impact tests and, in some cases, the Brinell hardness. These analyses have been selected to cover as wide a variation as possible within working limits and, in a few cases, special portions of heats have been shown in which the impact test fell below requirements.

Semisteel Requirements of U. S. Ordnance Department

It is perhaps fair to remark that there was some uncertainty as to just what was necessary in regard to the strength of shells to meet the requirements, so recourse was had to the tests developed in France for like purposes, with such modifications as it was thought would simplify their application to our system of weights and measures. It is probable that further study in actual service will be necessary before a system of tests can be devised that will, at the same time, safeguard the quality of the product and enable the manufacturer to produce satisfactory shells without suffering an abnormal penalty in rejected material. The tests, as finally outlined, were as follows:

Test-bar Casting.—Test bars shall be taken from the pouring ladle at each cast of approximately 2000 lb. and each bar shall be cast in a vertical mold of the same material as that in which the shells are cast. The cooling of the test bars shall be performed under the same conditions as the cooling of the shells.

Tensile-strength Test.—The test bar shall be cast 1.25 in. (31.7 mm.) in diameter, with a length of 8 in.(20.3 cm.) and a riser of 4 in. (10 cm.). At each end of the bar, for a distance not exceeding 2 in., the bar may be cast with a maximum diameter of 1.5 in. (38 mm.), in which case the riser shall be of the same diameter. After removal of the riser, the test specimen shall be machined at its central portion to a diameter of 1.128 in. (28.6 mm.) for a minimum length of 4 in. (10 cm.). The tensile strength of the specimen must be at least 32,000 lb.

Impact Test.—A test specimen 1.50 in. (38.1 mm.) square, and not exceeding 1.52 in. (38.6 mm.) on any side, shall be cast with a length of 8 in. (20.3 cm.) and a 4 in. (10 cm.) riser of the same area, between which and the bar there may be a neck of decreased area to permit the riser to be readily knocked off. After removal of the riser, the bar shall be placed on two angular supports having edges with a radius of 0.08 in. (2 mm.) and in turn supported on a one-piece anvil weighing at least 1750 lb. (793.7 kg.) and resting on a concrete or other solid foundation. A weight of 25 lb. (11.3 kg.), having its bottom curved on a 2-in. (50.8 mm.) radius, shall be caused to fall exactly on the middle of the test bar. The test shall begin with the weight at a height of 12 in. (30 cm.) and shall be repeated, always striking the same face of the test bar, with the height of the fall increased by ½ in. intervals until the bar breaks. The height of fall for causing rupture shall be not less than 18 in., this height being measured from the upper surface of the bar to the lowest part of the testing weight.

Hardness Test.—Hardness must not be less than represented by an indentation of 4.6 mm. diameter on Brinell machines at 3000 kilograms.

TABLE 1.—*Analyses and Tests of Semisteel*

Number	Mixture			Chemical Analyses								Physical Tests			Remarks
	Pig Iron Per Cent.	Steel Per Cent.	Remelt Per Cent.	Silicon Per Cent.	Sulfur Per Cent.	Phosphorus Per Cent.	Manganese Per Cent.	Graphitic Carbon Per Cent.	Combined Carbon Per Cent.	Total Carbon Per Cent.	Silicon and Total Carbon	Tensile Strength Lb. per sq. in.	Impact Test Inches.	Brinell Hardness at 3000 kg.	
1	39.4	25.2	35.4	1.04	0.118	0.100	0.76	2.57	0.65	3.22	4.26	35,570	19½	4.25-4.50 mm.	
2	40.5	24.8	34.7	1.15	.....	.....	0.72	....	....	3.22	4.37	33,380	17½		Third ladle
2A	40.5	24.8	34.7	1.01	0.101	0.080	0.80	2.60	0.62	3.22	4.23	38,510	20½		Thirtieth ladle
3	41.4	24.4	34.2	1.37	0.107	0.094	0.80	2.54	0.60	3.14	4.51	34,080	19		
4	40.5	24.8	34.7	1.26	0.104	0.092	0.81	2.50	0.63	3.13	4.39	37,630	18		
5	34.1	30.4	35.5	1.09	0.121	0.111	0.55	2.35	0.65	3.00	4.09	34,960	19		
6	34.0	33.0	33.0	1.10	0.109	0.108	0.64	2.13	0.71	2.84	3.94	46,960	18		
7	38.9	23.5	37.6	1.40	0.095	0.102	0.70	2.42	0.64	3.06	4.46	41,310	19	4.3 mm.	
8	39.2	23.4	37.4	1.01	0.100	0.118	0.66	2.32	0.67	2.99	4.00	41,490	18	4.1-4.3 mm.	
9	39.5	23.3	37.2	1.43	0.110	0.112	0.58	2.49	0.47	2.96	4.39	44,910	20	4.0-4.1 mm.	
10	34.4	32.8	32.8	1.28	0.123	0.104	0.60	2.36	0.66	3.02	4.30	49,030	17		
11	33.7	33.1	33.2	1.07	0.111	0.120	0.61	2.35	0.66	3.01	4.08	47,220	20		
12	38.9	23.5	37.6	1.38	0.102	0.102	0.72	2.45	0.61	3.06	4.44	32,810	15	4.1-4.2 mm.	
13	33.6	33.2	33.2	1.06	0.118	0.106	0.60	2.09	0.72	2.81	3.87	43,440	20.5		
14	36.7	21.9	41.4	1.61	0.119	0.120	1.10	2.51	0.60	3.11	4.72	37,840	16.5	4.0-4.1 mm.	

A study of Table 1, and other data accumulated during a considerable period of manufacture, indicate that the impact test is more or less erratic, as at present applied, and a few comparative tests made according to the United States specifications on bars made abroad and previously tested abroad according to French specifications showed a wide variation; and that the United States test is more severe than the French.

The statement has at times appeared that too high a tensile strength was not advisable, for the reason that, above reasonable limits, the impact test was likely to show a brittle iron and that the toughest iron was apt to be that which ran rather close to the lower limit in tensile strength. While this statement has been borne out in a very few cases in the operations upon which this paper is based, by far the greater number of cases show an increasing toughness with increasing tensile strength, as in the case of Nos. 11 and 13 of Table 1; no. 10 is one of the few exceptions mentioned.

There is a limit to which the tensile strength can be carried, however, for when the total carbon and silicon content falls much below 4.40 per cent., the semisteel becomes difficult to melt and is sluggish in the molds, so that slag and gases do not readily free themselves and defective castings result. For example, No. 13, in Table 1, shows a total carbon and silicon content of 3.87 per cent. While the tensile strength was above normal and the impact test showed good toughness, some of the test bars from this heat showed flaws from sluggish metal.

The total of carbon and silicon content below which it is unsafe to go is probably in the neighborhood of 4.00 per cent. It would not be wise to continue at this point for many heats in succession as, in addition to the liability to sluggish metal, there is danger of its "chilling white" unless carefully cooled, the more so as the remelt is returned day after day. The best results appear to lie between 4 and 4.40 per cent., with the total carbon remaining as near 3 per cent. as possible and the combined carbon at or near 0.60 per cent. Analyses 2 and 2A represent respectively the third and the thirtieth ladle from the same heat and are reproduced to show the tendency to weakness of the first metal from the cupola.

Cupola Practice

Second only to the necessity for careful chemical control is the need of a refined cupola practice, as it is easy to spoil an otherwise perfect mixture for semisteel, by lack of attention to details in melting. It is of the utmost importance that the coke bed be thoroughly ignited and leveled and that the charges be placed with the utmost care to maintain compactness and uniformity and a proper division between the coke and metal layers; the cupola should be kept filled to the charging door.

As the material composing the charges for semisteel has a greater

tendency to oxidation, it is important that careful attention be paid to the fluxing of the cupola. Limestone used alone is satisfactory, provided the heats are not more than 5 hr. in duration. It should be from 7 to 10 per cent. of the weight of the metal charge. A good depth of slag should be carried above the metal to admit of the thorough cleaning of the molten metal as it drips through this blanket of slag. For heats longer than 5 hr., it is advisable to substitute fluorspar for a portion of the limestone. From 15 to 20 per cent. of the weight of the limestone may be replaced satisfactorily by fluorspar on heats up to 10 hr. duration. It should be borne in mind, however, that fluorspar has about double the fluxing capacity of limestone in making the substitution, so that for every pound of fluorspar added, 2 lb. of limestone should be deducted.

It has been found satisfactory to place the charge of flux directly upon the coke. The steel, having a higher melting point than pig iron, should be charged immediately after the limestone, and it should be followed, in turn, by the pig iron and the remelt. The metal charge should be carefully leveled by filling the smaller pieces of the remelt into the crevices left in placing the pig iron.

More coke will be used in the melting of semisteel than is used in good gray iron practice, as the semisteel must come from the cupola extremely hot. Having a much lower carbon content, semisteel freezes at a higher temperature, and therefore needs to be handled at a higher temperature than gray iron. For the same reason, it should be handled rapidly and in large ladles to prevent too great a fall in temperature.

The great variation in composition, between the steel scrap used and the balance of the charge, necessitates a thorough mixing of the metal before pouring. To this end, it is advisable to make the charges as small as is consistent with pronounced separation of the layers of coke and metal in the cupola. This feature is also governed, to some extent, by the ability of the charging gang to maintain proper charging conditions. The smaller the charge, the greater is the difficulty in keeping the materials properly placed and the cupola full, so that it may become necessary to use slightly larger charges than would otherwise be desirable for the sake of maintaining the best charging conditions, especially in the case of heats of long duration. A cupola lined to 66 in. (167 cm.), operated very successfully on a 2000-lb. metal charge so long as the heats were of short duration but when the time was increased materially, it was found necessary to double the charge, using 4000 lb. of metal. In order to maintain proper mixing of the metal, a large mixing ladle is advisable, as well as large pouring ladles when as large a charge as the above is maintained.

A good melting practice for semisteel demands coke of good quality and a bed charge approximately 36 in. (91 cm.) above the top of the

highest tuyere opening; and coke charges between the charges of metal should range about 1 to 8 or 1 to 7.

Owing to the inferiority of the first metal drawn from the cupola, it is advisable to pig the first ton or two of metal melted. The reason for the inferiority of this metal can probably be attributed to several causes; among these are the greater oxidation, resulting in a low and uncertain manganese and silicon content and the tendency of the gray iron to melt ahead of the steel. It is, therefore, advisable to make separate analyses of the first metal, which is pigged for remelt, and to treat it as a separate constituent in calculating the mixtures. In order to render the variation in this first metal as small as possible, small steel scrap should be used on the first charge in order that it may melt as nearly as possible at the same time as the gray iron.

After the first ton or two of metal has been tapped into the mixing ladle, the cupola should be plugged and the ladle drained so that the subsequent metal will not be contaminated with the first metal drawn. When the metal is again tapped, it may be allowed to run continuously and the molten metal drawn from the mixing ladle into the pouring ladles as required.

The blast should be maintained at a uniform volume and of sufficient quantity and pressure to penetrate to the center of the melting zone. A satisfactory pressure for a cupola lined to 66 in. has been found to be from 14 to 16 oz., which will result when approximately 30,000 cu. ft. of air per ton of metal melted is supplied and the charges are compactly placed.

In regard to manipulation of semisteel during and after pouring, it is sufficient to state that standard foundry practice consistent with the best results in gray iron should be maintained.

DISCUSSION

W. J. MERTEN,* East Pittsburgh, Pa. (written discussion).—Although Mr. Hall claims excellent results and emphasizes that they were obtained through what he calls good cupola practice, the writer's experiences and also those of many other metallurgists in semisteel melting practice indicate the converse.

One of Mr. Hall's most astonishing assumptions for a successful melt is the necessity of elevating the coke bed to 36 in. above the tuyeres, or about 1 ft., above the hottest zone of the cupola, a fact that an analysis of the melting practice of his company readily proves. A charge of iron plus 25 per cent. steel for a 66 in. cupola, when properly bedded, should be very close to 4000 lb., provided the charge is lodged right within the melting zone, which is about 22 in. above the tuyeres. The exceedingly

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small charge of 2000 lb. for that size of furnace can only be explained by the abnormal position of the metal with respect to the melting zone The necessity for doubling the charge on a continuous run, or when the cupola lining becomes thoroughly heated, was induced by the underestimated weight of coke between the charges, a ratio of 1 to 8, or even 1 to 7, is a low rating; 1 to 6 is a more correct rating until the cupola gets hot. This undercharging lowered the upper extremity of the coke bed so as to bring it nearer, or within, the melting zone proper, and melting then proceeds more in accord with real cupola practice.

To pig a ton or two of the first iron is also indicative of a rather unusual practice, and no difficulty will be experienced in getting all the heat necessary to melt the steel and melt it hot, or as the term goes, "smoking hot," when the coke bed is at the right height. The extra foot of coke serves to keep the charge in the cooler region and consequently gets only heat enough to melt the iron and all comparatively low fusible materials of the charge, leaving the steel behind. The iron on its way down gets into contact with this extra amount of coke, absorbing from it an excessive amount of carbon and an extra percentage of sulfur and other impurities. It is readily conceivable that the iron is not fit to be poured into a shell mold; it is hardly fit for the commonest gray-iron casting.

Mr. Hall's table of analyses and tests shows sulfur contents higher than any semisteel specification will permit, and the conditions set forth as being responsible for this are the minor factors. The writer has had remelts of 40 per cent. or more and has kept sulfur down to 0.07 and 0.08 per cent. The writer has also melted 40 per cent. steel mixtures and was able to use every ounce of metal melted and has had uniform conditions all through the heat. He has at will varied the grade of semisteel castings from 40 per cent. mixtures to 25 per cent. steel, following the very first or the second charge, depending on the requirements of the foundry floor. But it requires skilful operation and handling of the cupola.

Table 1 of Mr. Hall's paper substantiates the observations and experiences of the writer with semisteel meltings; namely, a range of total carbon of 2.75 to 3.00 per cent. with silicon at 1.25 to 1.40 per cent., and manganese 1.00 per cent. minimum in a cylinder casting gives best results under impact and tensile tests.

The effort to improve the status of semisteel has been in vain. Semisteel of a decidedly higher quality has been made and used for diverse purposes for over 50 years in the United States, and for shells, shrapnel, and other castings abroad.

R. F. HARRINGTON,* Boston, Mass.—This so-called semisteel, in which possibly from 10 to 40 per cent. of steel is used in conjunction with

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pig iron in place of the usual cast-iron scrap, has always been of rather great interest to the speaker from the standpoint of its wear-resisting properties. We hear a great deal about the high tensile strength, transverse load, and increased deflection obtained through the use of steel, as compared to metal made without the use of steel. This is particularly true in the case of the frictional parts of the locomotive, where much material of both kinds mentioned is used. The acid test, so far as service is concerned, is to a great extent its wear-resisting qualities. A considerable tonnage of material is manufactured in what are known as gray-iron air furnaces or open-hearth furnaces; this material is used in castings where resistance to wear, toughness, and closeness of the sections are necessary. Through this type of furnace, similar properties are obtained in that the total carbon is reduced and the denseness of the material is greatly increased.

I have often wondered how the wear-resisting qualities of these two metals would compare; viz., a metal made through the use of steel and one through the use of the open-hearth or air-furnace type of melting unit. I know of no work in which an endeavor has been made to determine wear-resisting qualities of the one metal as compared to the other; in fact, I am unaware of any exhaustive work in which tests to determine the wearing quality of any cast iron have been made.

In the railroad world, considerable stress is laid upon this question of wear and many men believe that the addition of steel materially reduces the wearing quality of a metal, compared with a metal of the same analysis obtained through the reduction of carbon by other means. Some attention should be paid to the theory, as advanced by the practical man, and some effort should be made to test out the relative wear-resisting qualities of one metal as compared to another. Possibly the difference is so slight that its detection would be difficult.

HENRY D. HIBBARD, Plainfield, N. J.—The word semisteel is much abused, but there is nothing that takes its place. In the metallurgy of iron the term is used for a cupola product with steel for a part of the charge; the air-furnace product, where part of the carbon of the iron is worked out, making so-called gun iron; and iron for malleable iron castings. A little while ago I found that some dictionaries defined semisteel as puddled steel. Some other name should be devised for these products, some distinctive name, but that is too much to hope for now, as people use this term in connection with their products and customers have become accustomed to this name.

R. F. HARRINGTON.—Doctor Moldenke, in a talk before the Boston Section of the New England Foundrymen's Association about a week ago, said that it was necessary to show the public the difference between the so-called semisteel and a metal that contains 5 per cent. steel and one containing 50 per cent., especially if the same price is charged for both.

It seems to be the question of differentiating between a superior metal and one that possibly may have 5, 10, 15, or even 20 per cent. steel and is far from satisfactory.

CHAIRMAN RICHARDS.—One other product that may be classed with semisteel is the synthetic cast iron made in the electric furnace. During the war, Keller, Leleux & Co., of France, erected a large number of plants for manufacturing synthetic cast iron from the large amount of steel scrap and turnings at hand, and found that the work was well done in the electric furnace. The term "synthetic cast iron" is not bad, because it means cast iron that is partly manufactured in the process of melting.

THOMAS GILMORE,* JR., New York, N. Y.—Occasionally, I have use for molds made of white iron, but have found it practically impossible to get the kind of material desired from foundrymen. Though samples submitted by them are good, the material actually furnished will vary from an ordinary soft gray iron to sash-weight iron and yet a fine-grained bright crystalline iron has excellent wearing qualities when used in connection with very abrasive materials, such as flue dust, iron borings and steel turnings, especially where high pressures are applied and there is friction. Under such conditions, the above iron will compare favorably in wearing qualities with such materials as manganese or chrome-nickel steel, which are often used, and the cost is much less.

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Acid Open-hearth Process for Manufacture of Gun Steels and Fine Steels*

By W. P. Barba,† Philadelphia, Pa., and Henry M. Howe,‡ Bedford Hills, N. Y.

(New York Meeting, February, 1922)

Introduction by Comfort A. Adams**

When this country went into the war, but two concerns, The Bethlehem Steel Co. and The Midvale Steel and Ordnance Co., knew how to make steel fit for great cannons and at these concerns there were relatively few men who knew the whole art. Fortunately, certain of these men put their knowledge at the service of the Government, and proceeded to instruct the metallurgists at the arsenals and at various steel works.

Doctor Howe, then chairman of the Engineering Division of the National Research Council, suggested that this work might be facilitated, and the number of effective gun-steel makers thereby increased, if a detailed description of the best practice could be written, giving the reasons for the various steps, and issued with the endorsement of a committee composed of those who were evidently the most competent authorities. It was thought that something would be gained by clarification of the subject, and something by the eminent authority of the members of the committee. To that end, the Engineering Division appointed a committee, consisting of the gentlemen whose names follow, to mention only those who retained their connection with it.

At this time there were serious difficulties in the manufacture, for the Government, of aircraft and high-speed engine crankshafts, of certain ordnance forgings, and of shells for both the Army and Navy. This Committee was asked to study and report upon these, with a view to betterment of practice. There were indications that the source of some of the difficulties went back to the melting of the steel and the production of the ingot. Hence, the committee first studied steel melting and ingot production, in order to guide the wartime manufacturers to an even larger percentage of useful production from the steel initially melted.

Committee on Steel Ingots

W. P. Barba, chairman, Ordnance Dept., U. S. A. (formerly Vice Pres. & Gen. Mgr., Midvale Steel Co., Philadelphia).

George K. Burgess, Chief of Division of Metallurgy, U. S. Bureau of Standards, Washington, D. C.

Henry M. Howe, Then Chairman Engineering Division, National Research Council.

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* Report of Progress to the Steel Ingot Committee of National Research Council.

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E. F. Kenney, Metallurgical Engr., Midvale Steel and Ordnance Co., Philadelphia, Pa.
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Theo. W. Robinson, Vice-President, Illinois Steel Co., Chicago, Ill.
A. A. Stevenson, The Standard Steel Works Co., Philadelphia, Pa.
Bradley Stoughton, Secy., Amer. Inst. of Mining and Metallurgical Engineers, New York, N. Y.
W. R. Walker, Asst. to the President, U. S. Steel Corpn., New York, N. Y.
Frank D. Carney, of Carney & Lindemuth, Consulting Engineers, New York, N. Y.

The Committee deputed the authors of this paper to prepare the proposed report, which they did forthwith. This was a few weeks before the armistice in 1918. The paper was completed soon after, so that it represents the work of the authors in the autumn and winter of 1918, but its publication has been delayed by several causes.

General Outline of Report

In sections 1 to 11 inclusive, we give a condensed statement of our subject, in particular indicating the chief ends to be held in view in conducting the open-hearth process for gun steel, while in the remainder of the paper we elaborate this matter.

1. *Composition.*—In order to comply with the physical tests of American ordnance specifications, the composition of nickel-steel pieces for cannon and shafting should lie within the following limits, the exact composition varying with the part of the gun which the piece in question is to form, whether tube, jacket, hoop, or other.

	Per Cent.		Per Cent.
Carbon	0.35 to 0.50	Manganese	0.50 to 0.75
Phosphorus	below 0.05	Silicon	0.15 to 0.30
Sulfur	below 0.05	Nickel	2.50 to 3.75

For ease of exposition we have assumed a specific carbon content, 0.35 per cent.

The steel should be brought at the moment of teeming[1] to the desired composition in every respect.

(*a*) The manganese and silicon must be brought to the desired proportion. In order to do this, the bath should be freed from oxygen as nearly as possible and certainly to a constant degree. This freedom from oxygen is important also for lessening or preventing segregation, blowholes, and structural metallurgical weakness.

(*b*) Phosphorus and sulfur must be below the prescribed limit, and to this end the stock must be sufficiently free from them.

(*c*) The chromium and nickel must be within the prescribed limits.

2. *Temperature* must be accurately regulated, for reasons which will appear in the following paragraphs.

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[1] Throughout this paper *tapping* refers to pouring the steel from the furnace into the ladle, and *teeming* or *pouring* to pouring it from the ladle into the mold.

3. *Segregation* must be restrained, and to that end the steel must be poured at a relatively low temperature[2] and must be free from oxygen.

4. *Columnar crystallization* must be restrained and the size of the dendrites kept down. To this end the teeming temperature should be relatively low.

5. *Piping Must be Restrained.*—To this end the ingots should be cast with the large end up, and at as low a temperature and as rapid a rate as the ingot sizes and the chemistry of the steel permit.

6. *External Cracking Should be Prevented.*—Here we may note that there are two periods of brittleness. First, when the steel is cooling toward the solidus, and thus is a viscous solid, an intimate mixture of a large proportion of already solid pasty particles and a relatively small proportion of still molten steel. Second, at the blue heat. The tendency in any given layer to crack in this period is often exaggerated by the simultaneous expansion which the deeper seated and slightly hotter layers are undergoing in passing through the recalescence.

We guard against this external cracking.

(*a*) By tapering the mold so strongly that the ingot frees itself from it readily during the contraction period immediately after pouring, and hence is readily withdrawn.

(*b*) By pouring at a relatively low temperature and slowly, first so that as the molten steel rises in the mold, the thickness of the already solidified walls may increase fast enough to withstand the increasing ferrostatic pressure; and second, that the size of the columnar crystals and the dendrites may be restrained.

(*c*) By fluting or otherwise shaping the outer surface of the ingot, which has little power of stretching, so that it can bend horizontally and thus accommodate itself to the resistance of the slower cooling and hence slower contracting interior.

7. *Internal Cracks Including Flakes Must be Restrained.*—(*a*) By interrupting the relatively rapid cooling in the mold and replacing it with slower cooling in ashes as soon as the ingot has solidified sufficiently to be moved without danger of cracking. When the ingots are cast with the small end up, their molds may be stripped before they have cooled far enough to make it expedient to bury them in ashes. If this is done, the time between stripping and burying them forms a third portion of cooling.

(*b*) By saddening[3] and thereby toughening the ingot very carefully, so as to prevent cracking it mechanically in forging or rolling.

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[2] This represents American practice. In section 39, we consider the reasons which favor the opposite course of pouring at a high temperature, as is done in Continental Europe.

[3] To *sadden* an ingot means to substitute strong cohesion and toughness for its initial fragility due to its having a very coarse crystalline sugar-like structure. This may be done by giving it a succession of light reductions under a hammer or press, or in a rolling mill. "Sadden" is evidently closely related to "sodden."

(*c*) By retarding the heating of the ingot for forging and that of the forgings themselves, so as to lessen the thermal stresses.

(*d*) By as great freedom from inclusions as possible.

8. *Retention of Inclusions Must be Restrained.*—(*a*) By deoxidizing the molten steel as fully as possible by means of the carbon of the pig iron, because the product of its oxidation is gaseous and escapes, whereas those of all other deoxidizing agents are solid or molten and tend to remain as inclusions. In order that as much as possible of the deoxidation should be done by carbon, the working temperature during refining must be held as high as the safety of the roof will permit.

(*b*) The nearly complete deoxidation by carbon should be followed by further deoxidation by silicon. The manganese should not be added till after this silicon has done its work of deoxidation, in order that as little as possible of it may oxidize. This is both so that the manganese content of the product may be as nearly constant as possible, and that as little manganese oxide as possible may form to corrode the siliceous hearth of the furnace and form inclusions of manganese silicate with the silica so eaten away. This postponement clearly tends to lessen the oxidation of manganese; first, by shortening its stay in the furnace and, second, by pre-deoxidizing the bath with the silicon.

(*c*) The steel should be held in the ladle a moderate length of time to allow the inclusions to rise to the surface, and also for the much more important purpose of permitting the finished steel to fall to the proper temperature for casting into a successful ingot.

9. *Hot and Cool Pouring.*—American practice, which is the chief subject of this paper, may be summed up briefly as refining hot but pouring cool. We have now seen four reasons for cool pouring:

1. That it is thought to restrain segregation;
2. That it restrains the size of the dendrites;
3. That it lessens piping;
4. That it lessens or prevents external cracking.

On the other hand, it certainly favors the retention of inclusions, by shortening the time available for their rising to the surface in the ladle. Their opportunity to rise is really good only so long as the steel is completely molten. As soon as it cools to the liquidus, it ceases to be wholly molten and becomes an emulsion of an ever-increasing quantity of pasty particles of metal which have already solidified.

10. *The Furnace Itself Must Be Protected.*—To this end,

(*a*) Its hearth should be protected from iron oxide by covering it, before charging the scrap, with about half of the pig iron used.

(*b*) The working temperature of the furnace must be maintained during the melting and refining periods at the highest point consistent with safety to the furnace: First, so as to shorten the melting period, during which the hearth is exposed to the attack of the iron oxide, because

it is not fully covered by the molten charge; second, so as to stimulate the deoxidizing action of the carbon of the bath during the refining period.

11. *Recapitulation.*—There are really only four purposes served by these various precautions, with their many subprecautions, viz.: To make the ingots:

(*a*) of proper and uniform composition,

(*b*) of proper macro- and microstructure, and

(*c*) sound, that is free from pipes, blowholes, cracks, and roughness, and

(*d*) to prolong the life of the furnace.

Detailed Discussion of Report

12. *General Course of Acid Open-hearth Process.*—The foregoing sections teach that the general aim of the process is to melt and decarburize the initial charge; to remove the oxygen incidentally introduced in this decarburization; to bring the charge to a high temperature in order to favor the deoxidation; to push this deoxidation further by means of silicon; and to complete it by means of an addition of manganese sufficient both for this purpose and for leaving in the steel the manganese content required. While doing this last we lower the temperature to that suitable for teeming, taking care that the bath temperature remains so high that the manganese reaction may complete itself, and we then teem the steel into ingots free from inclusions and other mechanical defects. Thus we "refine hot but pour cool."

13. The *raw materials* of the acid open-hearth process are pig iron, scrap steel, and in standard American practice a little iron ore.

The ratio of pig to scrap is usually spoken of as if these two materials formed the whole charge. Thus the 40:60 ratio refers to the use of 40 parts, by weight, of pig iron to 60 parts of scrap apart from the small quantity of ore used. This 40:60 ratio is the one assumed in this report

This pig-scrap ratio varies widely from 100 parts of pig, as in the typical pig-and-ore or Siemen's process, to only about 10 parts as in some European practice. To this important ratio we will return in Sections 33 to 35, after fixing our ideas by considering the standard American practice, which is the chief subject of this paper, and the Continental practice. Suffice it here to say that, as the function of the ore is to oxidize the silicon and the excess of carbon over that needed in the product plus that incidentally removed in the necessarily strongly oxidizing process itself, the quantity of ore used increases with the ratio of pig to scrap, from zero in the typical French and Italian non-oring low-pig practice to the large quantity needed for carrying out the typical pig and ore process.

Not more than 10 per cent. of the whole charge should be in the form of turnings, lest the rapidity and the indeterminateness with which they

oxidize introduce an indeterminate quantity of iron oxide into the charge. Here, as in all other respects, the working conditions should be brought as nearly as possible to a fixed standard, because it is difficult to compensate for the results of even minor variations in procedure.

When pig iron is relatively expensive it may be replaced partly, or even wholly, as a means of introducing the needed carbon, by charcoal, anthracite, or petroleum coke, when these latter may be had sufficiently free from sulfur.

14. *Method of Charging.*—Half the pig iron should be spread upon the hearth, the scrap should be placed upon this, and the other half of the pig iron on top of the scrap. The reasons for this arrangement are, first, that the hearth should be protected by a layer of pig iron from being cut by the oxygen-bearing drops of molten scrap. As this molten metal trickles down, drop by drop, over the oxidized surface of the scrap immediately beneath, it is almost certain to become strongly charged with oxide, and hence to corrode the bottom, unless this is prevented by causing it to trickle over a layer of pig iron below it. The carbon and silicon of this pig iron will, of course, react energetically with these drops of molten oxygen-bearing iron, to deprive them of their oxygen.

Second, the purpose of covering the scrap with the remainder of the pig iron is to protect it from the cutting effect of the flame, which thus is utilized for oxidizing the carbon and silicon of the pig iron, instead of being employed viciously to oxidize the scrap and, thereby, to cause it to attack the hearth and poison the bath with oxides, as just indicated.

15. *Composition of Charge.*—The carbon content of a charge of 40 per cent. pig and 60 per cent. scrap is about 2 per cent. In melting, this should fall to about 1.25 per cent.

16. *Phosphorus and Sulfur.*—For gun steel, the content of these impurities should be as low as possible, hardly over 0.05 per cent. of each. In the case of small ingots, less than 26 in. in diameter and weighing less than 15,000 lb., a very slight increase in the phosphorus and sulfur content might be considered, but not in the case of large ingots, because in these the local concentration of phosphorus and sulfur, both in the axial segregate and in the interdendritic or local segregates, more easily causes a prohibitorily large content of these impurities locally, resulting in black ghost lines.

17. *Manganese.*—(*a*) It is well that there should be from 1 to 1¼ per cent. of manganese present in the initial charge. Some of this oxidizes during melting, but an appreciable amount remains in the molten metal and aids both in the removal of sulfur in the form of manganese sulfide and in lessening the oxygenation of the bath. By this latter effect, it lessens the loss of manganese in the final additions.

(*b*) This restriction of the oxygenation of the bath, even to the end of the process by an initial manganese content as small as 1 per cent., is

surprising. The intensity of the deoxidizing conditions needed in making ferromanganese in the blast furnace shows how readily manganese oxidizes; hence we should expect the initial manganese to be oxidized rapidly during the oxidizing stages, both in melting down when the upper half of the pig iron trickles down drop by drop over the oxidized crusts of the metal beneath it in a strongly oxidizing atmosphere, and also in the intentionally oxidizing stage, Period II.

18. *Nickel.*—The nickel content of the initial charge should be somewhat less than that required in the final product, so that it may be rectified by additions of nickel at a convenient stage in the process. Rectifying by the subtraction of nickel is, of course, impossible.

19. *Chromium.*—Unless chromium is absolutely required by the specifications, it is advised that not more than 0.05 per cent. of it should be present in the mixture, because of the difficulty of overcoming its tendency to cause inclusions and consequent laminations. Chrome steels, as such, are not discussed here.

20. *Graphical Representation.*—Fig. 1 is an attempt to express the various stages of this process graphically. Vertical distances represent temperature, and horizontal time. For convenience, the process may be divided into five periods as follows:

I. Melting the charge.

II. Accelerating the oxidation of the carbon in excess of that needed in the product by oring and raising the temperature to the high point needed for the ensuing deoxidation of the metal.

III. Carrying the deoxidation as far as this can be done by means of the carbon of the bath and high temperature.

IV. Carrying the deoxidation still farther by adding ferrosilicon while the bath is still at a high temperature and cooling.

V. Continued cooling, adding ferromanganese, to complete the deoxidation and give the product the desired manganese content, tapping, and teeming.

21. *Period I, Melting.*—(*a*) In the first period, the liquidus *BC* refers to the average melting point of the charge from time to time. The melting point of the scrap is, of course, much above that of the pig iron.

(*b*) The more strongly curved line *AA* represents the actual temperature of the metal. Starting completely solid and at room temperature at the origin, it rises gradually during the first period, at the end of which it crosses line *BC*, so that the actual temperature of the metal coincides with its liquidus, or temperature of complete fusion.

(*c*) The rise of temperature should be as rapid as possible so as to shorten this period, in the early part of which the hearth is attacked more or less seriously by the oxide of the melting metal which trickles down.

22. *Period II, Oring.*—(*a*) When the charge is completely melted,

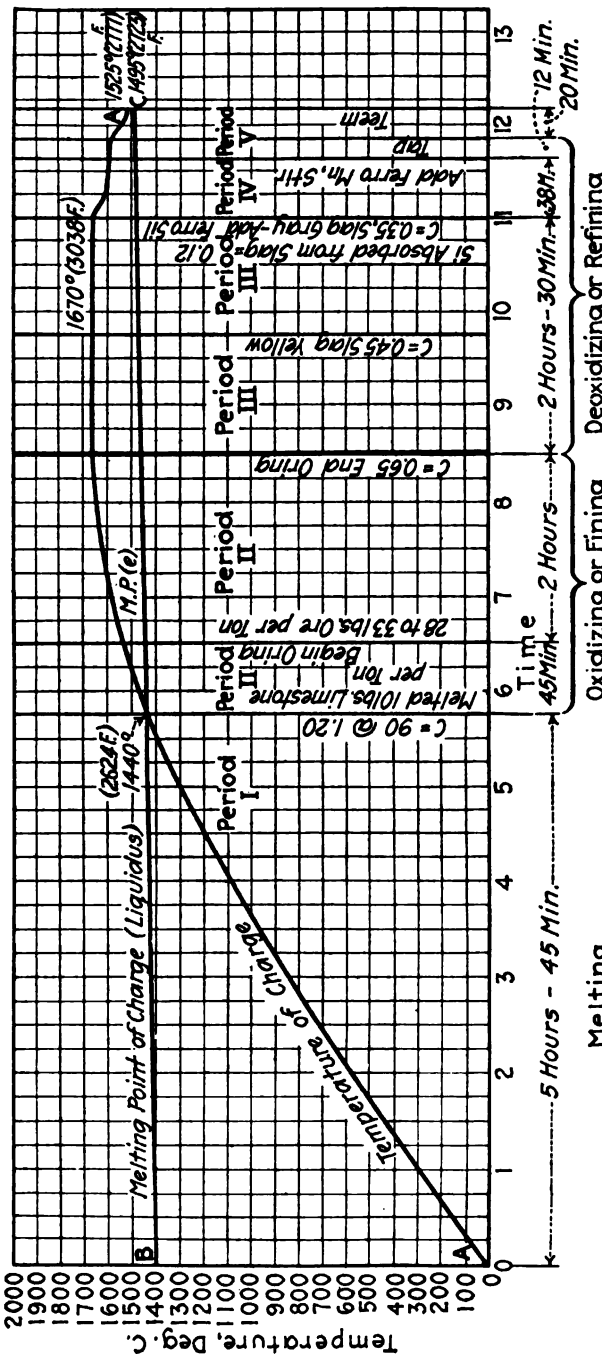

FIG. 1.—APPROXIMATION TO A TIME-TEMPERATURE DIAGRAM OF THE ACID OPEN-HEARTH PROCESS ON GUN STEEL.

it should contain 0.90 to 1.20 per cent. of carbon. We have now to remove this carbon rapidly. The first step is to add about 10 lb. of limestone per ton of charge, both that the slag may be fluid and that the carbon dioxide given off may start the metal boiling. This boiling should continue from this point on until very near the end of the process, in order to transfer to the lower part of the charge the heat reflected from the roof against the slag floating on the metal. It has often been proved that a "quiet bath" may be very heterogeneous in composition. If the circulation is not sufficiently rapid, it should be assisted chemically or mechanically. Mechanical stirring with rods is most beneficial from every point of view and is usual.

What may be called "chemical stirring" is that brought about by the evolution of carbon dioxide from the limestone and of carbon-monoxide gas within the bath itself by the reaction between the iron oxide in the slag and in the metal with the carbon of the metal. This reaction is brought about by the introduction of iron ore, or "oring."

(*b*) In about 45 min. after complete fusion, the charge should be so hot that we may begin oring. The quantity of ore needed is usually 28 to 33 lb. per ton of charge and is usually added in several portions. A rich, pure, low-phosphorus Lake Superior hematite may well be used. The ore should not be charged before the metal has passed so far above its liquidus that there is no chance of its being locally so chilled by the ore itself, and by those features of the reaction which are endothermic, that this reaction will not take place actively. Hence the very considerable gap between lines *AA* and *BC* when the oring begins.

(*c*) At about 2 hr. and 45 min. from the beginning of Period II, the carbon should have fallen to about 0.65 per cent. This should bring this period to a close, because the time between the arrival of the carbon at this content (0.65 per cent.) and its arrival at the final content (0.35 per cent.) is only about enough to insure an approximately thorough removal from the charge of the oxygen which has incidentally been incorporated into it in this second or oring period.

23. *Period III, Deoxidizing or Refining by Carbon.*—The object in this period is to carry on the removal of the oxygen from the metal by means of the carbon still present, and of the very high temperature which gives that carbon its needed energetic action on the oxygen. The observations of Doctor Burgess indicate that the temperature of the metal at this time is about 1670° C., which is about as high a temperature as the metal can be brought to without endangering the roof or shortening its life unduly.

24. *Appearance of the Slag.*—We have, at present, no direct means of following the removal of the oxygen from the molten metal, nor indeed do we know how much residual oxide is compatible with the needed excellence of the product. Instead we rely on the removal of iron oxide

from the slag, on the principle that as the iron-oxide content of the metal falls, that of the slag decreases with it. And, in general, the iron oxide distributes itself between metal and slag in proportions tending to reach an equilibrium, the ratio of which doubtless varies with the temperature, the carbon content of the metal, and other conditions.

Fortunately, the appearance of the slag gives so close an indication of its content of ferrous oxide that the open-hearth process need not be held back to allow a direct chemical determination of that oxide to be made. This appearance may be noted in a slag cake about ¼ in. deep and 3 in. in diameter. But such cakes are seldom made, because sufficient information can be had from the thin layer of slag which adheres to the shank of the test ladle used to secure the many samples of metal required for observation during the process. The outer surface of this slag is dark brown, like that of glazed drain tiles, probably because its ferrous oxide is converted into ferric oxide in passing through the air. The cross section is rather waxy. The steel makers speak of its having an increasing degree of vitreousness as the ferrous-oxide content of the slag decreases. To the layman, it suggests rather an increasing degree of waxiness. But with this understood, we may speak of its vitreousness.

The color of the interior of the slag sample, apart from the rather constant dark brown of the crust, is, next to its vitreousness, the best indication of the progress of deoxidation. A slag rich in iron oxide, and hence overlying a bath rich in oxygen, is dark brown to black. As the oxygen is removed from the metal and the ferrous oxide from the slag, this color grows continuously paler, to a yellow, a gray, and if the deoxidation is complete in the electric furnace, even to a white.

By the middle of Period III, when the carbon content has fallen to about 0.45 per cent., the ferrous-oxide content of the slag should be reduced to about 18 or 20 per cent., and its color should be a clear, pale lemon yellow in the case of a charge initially nearly free from manganese; and of a like tint, but more greenish, in the case of a charge containing initially about 1 to 1¼ per cent. of manganese, as indeed is very desirable. The manganese oxide adds a strong greenish cast and sometimes a dark greenish central "streak" to the color which the ferrous oxide gives itself. In this case the ⅛ to 3/16 in. thick section of the slag sample has five differently colored layers, two dark brown outer ones, then two of the characteristic yellow, then a central darker cloudy greenish "streak," merging into the yellow ones.

25. *Period III, Continued.*—In the remaining half of Period III, the continuing removal of the iron oxide is recognized by the change in the color of the slag from yellow toward gray, in case the charge contained initially 1 to 1¼ per cent. of manganese. This color indicates that the ferrous oxide of the slag has been reduced to about 15 per cent., and this in turn that the metal is as thoroughly deoxidized as it can be by the

action of its carbon alone. The color and the texture of the slag referred to are typical only of the average practice, and both are affected by the volume of the slag, which depends, first, on the content of silicon and manganese in the charge; second, on the rapidity with which the charge is melted; and third, on the character and composition of the bottom.

During Period III, a certain quantity of silicon is reduced from the slag by the carbon of the metal, which should now have a silicon content of about 0.12 per cent. This increase in the silicon content of the metal, at least up to 0.12 per cent., is recognized by a progressively increasing compactness of the test ingots of the metal and their freedom from gas cavities. This, in turn, is due rather to the decrease of iron oxide in the metal than directly to the increase of silicon content. It has been reported, lately, that the silicon content of the metal at this point, as determined by chemical analysis, may include an important quantity of silica. One of us has good evidence that, in good practice, the increase of silicon content is not merely apparent but real, and any content of silica is negligibly small.

26. *Period IV, Deoxidizing by Silicon.*—(*a*) A sample of metal is now taken for the "go ahead" test, that is, a test ingot for a combustion determination of the carbon present in the charge. This test should show that the carbon is now about 0.35 per cent., or very close to that aimed at in the final product, so that we may safely go ahead with all preparations for tapping. To insure that the carbon in the product will be very close to that found in the "go ahead" test, we now arrest the decarburization by two distinct steps. First, at the time of drawing this, we make an addition of ferrosilicon, which will be attacked by any oxygen still present in preference to the remaining carbon. After this we decrease the temperature by lowering the damper and shutting off the air and gas, so that the only circulation through the melting chamber is due to leakage. We here act on the principle that the oxidation of the carbon is favored by a high temperature and opposed by a low one, as is well known to be true in the Bessemer process. A visible drop in temperature is shown at once by the changed appearance of the surface of the slag which, by the time the laboratory reports are received, will probably show a few dark cool points.

(*b*) The ferrosilicon, which may be of the 11-per cent. silicon grade, is added while the temperature is still so high that it melts almost immediately and quietly, that it attacks quickly any oxides remaining, and that the resultant silicates coalesce readily, rise to the slag, and leave the bath, which becomes very quiet, and practically ceases bubbling.

(*c*) The cooling must not go so far as to interfere with the prompt melting of the ferromanganese in Period V, and its reducing any residual oxide. The precaution is easy to carry out successfully.

27. *Period V, Adding Ferromanganese and Tapping.*—(*a*) At the end of about 38 min., Period IV comes to an end, and by this time the ferrosilicon should have completed, as far as it can, the deoxidation of the metal. We now charge the ferromanganese. This addition is purposely delayed until the bath is thoroughly deoxidized, in order to prevent any considerable loss of manganese, primarily in order that the small loss of manganese may testify to the thoroughness of the deoxidation caused by the action of temperature and carbon in Period IV, and secondarily because any considerable loss is likely to be an indeterminate one and thus to lead to irregularities in the composition of the product. Of this manganese, a very small quantity may be consumed in still further reducing the ferrous oxide of the metal, but most of it remains in the metal, giving it the physical qualities called for. At the end of about 12 min., the diffusion of manganese should be so complete that we may tap the charge into a ladle, in which the temperature falls still further, nearly to the liquidus. The steel is held in the ladle long enough, say 20 min. for 60-ton charges which are to be poured into very large ingots, to bring it to the relatively low temperature which is desired in American practice, as explained in Sections 37 and 38. We now teem. This brings us to the end of Period V, and therefore, to the end of the whole operation.

28. *Indications for Period V.*—The reduction of the ferrous-oxide content of the slag to 15 per cent. or less and the change of its color to gray at tapping time are trustworthy indications that the deoxidizing work of the process has been thoroughly done. In order that this may occur with the normal rate of decarburization, the ferrous-oxide content of the slag should have fallen at least as low as 18 per cent., and it should be yellow, when the carbon content of the metal has fallen to 0.45 per cent. These numbers refer to normal standard conditions, especially as to the weight and composition of the slag, and they may be changed materially by any one of various departures from the normal. For instance, to "run" or melt the roof seriously adds silica to the slag, and by thus diluting its iron oxide lightens its color.

But if the initial charge contains about 1 to 1.25 per cent. of manganese, as is to be desired, the resultant manganous oxide of the slag affects these colors decidedly, giving them a greenish tint. Under these conditions, a proper degree of removal of ferrous oxide is indicated if the slag is greenish yellow when the carbon content of the metal has fallen to 0.45 per cent., and greenish gray at tapping time. This greenish yellow slag may contain 15 per cent. or less of FeO.

29. *Loss of Manganese on Addition of Ferromanganese.*—(*a*) A further and extremely important indication that the metal has been thoroughly deoxidized before the ferromanganese is added is given by the loss of manganese in this reaction, which should not much exceed 10 per cent. of the added manganese. At some well-conducted works, after adding 0.73

per cent. of manganese to a bath containing 0.10 per cent., there is found in the ingots about 0.65 per cent., representing a loss of 0.18 per 100 of steel, or 4.61 per 100 manganese.

(*b*) Such inferences from the loss of manganese can be trustworthy only when the conditions in general, and in particular the time between adding the ferromanganese and determining the residual manganese, are strictly constant.

(*c*) If a larger proportion of the added manganese is lost, taking into account the length of time between adding ferromanganese and teeming, it is good evidence that the ferrous oxide had not been thoroughly removed from the steel. It is recommended that this point be watched with great care.

30. *Reasons for Procedure in Deoxidizing Bath of Molten Steel.*—(*a*) At the end of the oring, Period II, the bath of molten steel is richly charged with oxygen, probably in the form of ferrous oxide FeO, and the next task is to remove this oxygen as completely as possible. This means transferring the oxygen from the ferrous oxide to one or another agent, such as carbon, silicon, or manganese, each of which in its turn becomes oxidized. The procedure should be such as to cause as much of this oxygen to be removed by carbon and as little as possible by silicon and manganese, because the oxide of carbon is gaseous and escapes spontaneously, whereas those of silicon and manganese are molten. They are liable to remain entangled in the solid metal in the form of inclusions, which weaken and embrittle it greatly.

(*b*) In order that as much as possible of the oxygen should be removed by the carbon, it is necessary to work at as high a temperature as possible, because the power of the carbon to combine with the oxygen increases with the temperature. Hence the temperature of the metal is raised as rapidly and as high as is consistent with safety to the roof of the furnace.

(*c*) As the quantity of iron oxide remaining in the bath decreases, the carbon of the bath, finding itself no longer fully occupied in deoxidizing iron oxide, attacks the silica of the slag and hearth, introducing silicon into the molten metal. By the time that this action has raised the silicon in the bath to about 0.12 per cent., the power of the carbon to remove further oxygen has become so far exhausted that the further deoxidation of the dissolved iron oxide by this carbon has become so slow that it becomes expedient to use a stronger deoxidizing agent. Our choice naturally lies between manganese and silicon.

(*d*) In the acid open-hearth process, to which this paper refers, silicon should be used here, chiefly because the silica which it forms does not attack the hearth of the furnace as the manganous oxide resulting from the use of manganese does, forming manganese silicate.

It is true that, in careless hands, the use of silicon may cause the formation of very harmful inclusions of silica, but if the care and skill

appropriate to the manufacture of cannon steel are used we believe that this danger can be avoided fully. Of course whatever deoxidizing agent we use we must provide for the removal of its oxidized products. In the case of carbon, these products escape spontaneously because they are gaseous. In the case of manganese, they escape readily because the resultant silicates of manganese are fusible over a wide range of composition, so that they coalesce easily into masses so large that they rise quickly to the surface by gravity. But the product of the oxidation of silicon, silica, is infusible by itself at the open-hearth temperature. Hence should any of it remain uncombined with metallic oxides its individual particles would stay suspended as a fine emulsion and, persisting in the finished product, injure it greatly. Hence the use of silicon presupposes the presence of enough oxide of iron or manganese to form with the resultant silica a fusible and hence a coalescing product, which will remove itself freely by gravity. This is in harmony with the general procedure, using silicon for nearly but not quite the last of the deoxidation, when the resultant silica finds residual oxides to combine with, and then completing the deoxidation with manganese, the products of the oxidation of which are fusible and hence self-removing.

(*e*) Moreover the quantity of silica resulting from the removal of one part of oxygen from the molten metal by silicon is clearly far less than the quantity of manganese silicate resulting, first, from the oxidation of manganese to manganese oxide by that oxygen, and, second, from the formation of manganese silicate by the scouring action of the manganous oxide on the hearth.[4]

That manganese silicate does form, if manganese instead of silicon is added at this stage, has been proved directly by dissolving quantities of the resultant metal large enough to yield enough inclusions for chemical analysis.

(*f*) A welcome effect of the silicon added at this stage, when the oxygen content of the bath has become so low, is that it practically arrests the oxidation of the carbon, probably by combining by preference with that oxygen. Indeed, we now have the appearance of complete equilibrium, with no further transfer of any of the elements present from metal to slag. This arrest of the progressive oxidation of the carbon, manganese, and silicon simplifies the conduct of the process by assuring us that the content of these elements found in the "go ahead" test will persist and

[4] One part of oxygen would yield by the reaction $2O + Si = SiO_2$ $(2 \times 16 + 28.4) + 2 \times 16 = 1.9$ parts of silica; whereas by the reaction $O + Mn + SiO_2 = MnSiO_3$, it would yield $(55 + 28.4 + 3 \times 16) + 16 = 8.2$ parts of manganese silicate if of that composition, or about four times as much. Indeed the difference in favor of silicon is likely to be still greater, because each molecule of manganous oxide being released in the presence of an unlimited excess of the silica of the hearth, is likely to combine with more than one molecule of that silica.

occur in the ingots, practically undiminished in the case of carbon, and but slightly diminished in that of manganese.

(*g*) Parenthetically, in operating on a basic hearth, whether that of a basic open-hearth furnace, or that of a basic electric furnace, reasoning the converse of that in Section 30 (*d*) and (*e*) leads us to use manganese instead of silicon for removing the bulk of the oxygen left at the end of Period III, when the carbon has done its work of deoxidation as thoroughy as it can. The removal by silicon of the oxygen left at this stage would yield silica, which would attack the basic hearth, corroding it and thereby yielding inclusions of silicate of lime, magnesia, or whatever bases constitute the hearth. As before, the quantity of these inclusions of silica plus base, resulting from the removal by silicon of a given quantity of oxygen from the metal, would exceed the quantity of manganous oxide formed in performing that same deoxidation by means of manganese.[5] Attention should be called to recent practice where ferrosilicon is used as a preliminary addition in basic steel melting both in open-hearth and in electric furnaces with basic hearths.

(*h*) Returning to the study of the acid open-hearth process, manganese in the form of ferromanganese is now added and stirred in, both to push still farther the removal of oxygen from the bath and to give the metal the intended manganese content.

(*i*) Looking back on this deoxidation as a whole, we note first that carbon is the most desirable deoxidizing agent, because its oxides are gaseous and cannot form inclusions; second, that silicon is next in merit in acid furnaces, because it leaves less inclusions than manganese; and third, manganese is the last addition to make in such furnaces, because it is the strongest and can remove most of the remaining oxygen.

(*j*) Accordingly, by maintaining a very high temperature we enable the carbon to do as much as possible of the work of deoxidizing. We then use silicon to do as much of the remaining deoxidation as it will; and only then do we add manganese to complete the little deoxidation still to be done, and to give the product the needed manganese content.

(*k*) It is interesting that the manganese silicate formed on adding ferromanganese to imperfectly deoxidized steel is more abundant in the deeper seated parts of the ingot, especially of large ones, than in the crust, probably because of the fusibility of the manganese silicate itself. In

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[5] One part of oxygen removed by the reaction $O + Mn = MnO$ would yield $(55 + 16) \div 16 = 4.4$ parts of manganese oxide, whereas if removed by the reaction $2O + Si + 3CaO = Ca_3SiO_5$ it would yield $(3 \times 40.1 + 28.4 + 5 \times 16) + 2 \times 16 = 7$ parts of lime silicate if of that composition.

The numbers of course have no claim to precision. They are based on the assumption that tricalcic silicate results, with nearly three parts of lime to one of silica, which agrees with H. H. Campbell's analysis of basic open-hearth slag. ("Manufacture and Properties of Iron and Steel," 205. 1907.)

short, this silicate migrates like the segregating elements, carbon, phosphorus, and sulfur. In such steel, an excessive quantity of this silicate forms, because the abnormal quantity of oxygen present in the bath oxidizes a correspondingly great quantity of manganese to manganese oxide, which in turn dissolves from the hearth a correspondingly great quantity of silica.

This concentration of the manganese silicate in the deep-seated, and therefore last solidifying, parts may be referred jointly to segregation proper, and to the greater length of time available there for the coalescence of the manganese silicate, under the churning action of the convection currents in this imperfectly deoxidized, and hence wild, steel, into particles large enough for detection. This coalescence, though it would not affect the quantity of the manganese silicate found by chemical analysis, would increase that detected by the microscope.

31. The *use of aluminum, titanium, vanadium*, and like deoxidizers for the specific purpose of removing the last of the oxygen from the bath, as distinguished from their legitimate and growing use for introducing some of these elements as essential constituents of an alloy steel, should be discouraged. It affords so easy a way of covering up imperfect deoxidization in the normal way, chiefly by carbon, then by silicon, and last by manganese, as to form a constant temptation to slovenly working, and especially to slighting the thorough deoxidation by carbon at a prolonged high temperature. The oxide products of deoxidation by these elements are not gaseous, and hence tend to form inclusions. We do not discuss the manufacture of alloy steels other than nickel steel.

32. *Continental Low-pig Process.*—Instead of using about 40 per cent. of pig iron, as in the American practice just described in Sections 7 to 20, and thus having in the bath when first melted far more carbon than is needed in the product, then removing this excess of carbon with ore, and then removing the oxygen introduced by this ore, the typical French and Italian practice is to use much less pig iron, sometimes so little that the charge when first melted has only about 0.10 to 0.20 per cent. more carbon than is needed in the product. In this practice, the use of ore is avoided altogether, because the slight excess of carbon present will be removed spontaneously in bringing the charge to tapping temperature, by the action of the furnace atmosphere and of the iron oxide which is taken up during melting, and distributes itself between metal and slag in proportions approaching equilibrium. Thus here, quite as in American practice, metal and slag contain iron oxide which has to be removed. Part of this removal is done by such excess of carbon as there is, but if this excess is very small, it has to be helped out by adding pig iron in some works, coke in others, and both in still others.

The pig iron is added when the carbon has fallen to about that sought in the product, and the work of deoxidation then proceeds by

means of the carbon and silicon thus introduced. In some works, a second and even a third lot of pig iron is added when the carbon content again falls to the point sought.

Coke, when added, rests on the slag, and deoxidizes it directly. In some works, the slag is given a predetermined composition favoring its deoxidation, and through this the deoxidation of the metal, by additions of lime and limestone, clay, sand, and fluorspar to give fluidity.

These steps should enable us to make use of coke as an additional and very energetic remover of iron oxide. For, instance, in some French works, the coke treatment is continued not only until the slag is green, but until the iron oxide has been so far removed from the metal that it hardly reacts at all on the carbon, and hence the bath is completely quiet. Even after this, the charge is held for 1 hr. at a very high temperature to allow the inclusions to rise, and the removal of the iron oxide to progress still farther.

33. *Advantages and Disadvantages of Oring.*—(*a*) Now that we have examined at length, Sections 7 to 20, the standard American high-pig or oring practice, and have glanced, Section 32, at the Continental low-pig or oreless practice, let us here bring together on one hand the advantages of oring, that it enables us to use a larger proportion of the sometimes cheaper source of iron, pig iron; that it facilitates the process, by means of the boil which it induces; and that it increases the yield; and on the other hand its disadvantages of introducing into the molten bath iron oxide which must needs be thoroughly removed. Here, too, we should look at the advantage of high-pig practice, that in it the slag color is a more trustworthy indication of the condition of the metal; and at its disadvantages, that in it there is a thicker blanket of slag interposed between what might be called the two working surfaces, that of the metal and that of the slag itself, and that it works more slowly than low-pig practice.

(*b*) It is self-evident both that oring enables us to increase the ratio of pig to scrap and that this, in and by itself, is desirable if pig iron is cheaper than scrap. In arriving at their true relative cost, we may be influenced by the existence or lack of a supply of molten pig to pour into the open hearth, by the slower working in high-pig practice, and by like considerations. In American open-hearth works, it is rare that pig is enough cheaper than scrap to make it truly economical to use appreciably more than the 40:60 ratio, which we have advised for steel of this carbon content.

(*c*) A second merit of oring, and the high-pig practice in which it is used, is that the oxygen of the ore, in oxidizing the excess of carbon of the charge, keeps the charge in rapid ebullition, and thus simplifies the melter's difficult task of keeping his roof within the narrow range of temperature between that needed to heat the charge hot enough through

and through, and the only slightly higher temperature which would destroy the roof.

The boiling carries down into the metal and through it the heat reflected upon the upper surface of the slag from the flame and the roof, thus both heating the metal and cooling the roof. If the bath is still, this heat is in large part reflected back from the slag to the roof.

Because the difficulty of this transfer of heat from roof and flame to metal increases with the thickness of the slag layer, the boil is especially needed when there is much slag; that is, in high-pig practice, in which the silica from the ore and from the oxidation of the silicon of the pig implies a correspondingly great quantity of slag. This consideration cautions us not to claim undue weight for the boil as an advantage of the high-pig oring practice, remembering the obvious reply that it is this practice itself that gives the boil its importance, both for transferring the heat into the metal and for making the metal effectively accessible to chemical treatment applied to the upper surface of the slag.

(*d*) The oxygen of the ore, in oxidizing the carbon and silicon of the pig iron, leaves the iron with which it is initially united, by such reactions as $Fe_3O_4 + 4C = 3Fe + 4CO$. Part of the iron so left adds itself to the molten bath and so increases the yield of iron. In making fine steel, this saving is rarely of great moment in comparison with the features of the practice which influence the quality.

(*e*) Turning from the merits to the disadvantages of the high-pig or oring practice, the thicker blanket of slag which it implies, as shown in (*c*), may reasonably be held to oppose the complete deoxidation of the bath, so essential to high quality; for the oxygen strives ever to distribute itself between metal and slag in a ratio, fixed for given conditions even though varying with the conditions, so that the metal can be deoxidized only as the slag is.

Moreover, this equilibrium ratio is not between the total quantity of oxygen in metal and slag, respectively, but between the percentage of oxygen in each, so that the percentage to which the iron oxide of the slag must be lowered in order to bring about a given thoroughness of deoxidation of the metal is independent of the quantity of slag. Hence, the more slag there is the greater is the work of deoxidizing it thoroughly enough to induce a given thoroughness of deoxidation of the metal. It may be that the thoroughness regularly attainable is inversely as the quantity of the slag, a small quantity being susceptible of more thorough deoxidation than a large one.

(*f*) The objection which is urged strongly against oring, that which seems to have led to its exclusion from the standard French and Italian practice, is that, by introducing oxygen into the molten metal, it increases the difficulty of thorough deoxidation, and indeed lessens the practicable thoroughness of deoxidation of the metal.

These two objections (*e*) and (*f*) may well be taken together, as two aspects of a single objection. Their validity is not self-evident. To deoxidize a greater quantity of slag as thoroughly as a smaller one should indeed take longer, but it does not follow that the practicably attainable thoroughness of deoxidation is less with the larger quantity. Again, in purification of any kind, whether by washing or deoxidation, it is the last stage, the final degree of thoroughness, that calls for the technical skill. The greater the needed thoroughness of deoxidation, the stronger must be the deoxidizing conditions.

But while the validity of these objections is not self-evident, neither is their invalidity. Rather than belittle or ignore them we should diligently seek evidence as to their true weight. Such evidence should be found in the iron-oxide content of the slag, and the physical properties of the steel, in oring and in oreless practice respectively, though in this comparison it is hard to make the oring the sole variable.

The thorough purification of the metal from oxygen, both that formed in melting and any introduced as ore, needs indeed our most careful attention, as is shown by the length at which we describe it in Sections 23 to 30.

34. *Appearance of Slag in Oring and Oreless Practice.*—American metallurgists have found a serious objection to low-pig practice in the diminished trustworthiness of the appearance of the slag as a guide to the thoroughness of the deoxidation of the metal. The reason for this is evident. In the American practice, it is the metal itself that, through its carbon and silicon, initiates the removal of ferrous oxide. These deoxidize the ferrous oxide in the metal and thereby induce a corresponding removal of ferrous oxide from slag to metal, following the principle that this oxide always tends to distribute itself between slag and metal in an attempt to approach equilibrium. Hence the removal of iron oxide from the metal here precedes its removal from the slag, and hence a certain degree of removal of this oxide from the slag, as indicated by its color, is trustworthy evidence that the corresponding removal from the metal has already taken place.

But when we proceed by adding coke, or other form of carbon to the slag, it is in the slag that the removal of iron oxide is initiated. Only after the coke has begun removing this oxide from the slag does the iron oxide in the metal rise into the slag to replace, in part, that which the slag has just lost, in the attempt to approach an equilibrium distribution of the oxide between slag and metal. Here, then, the removal of iron oxide from the slag precedes that from the metal and may precede it materially. Thus a given thoroughness of removal of iron oxide of the slag is not such good evidence that the corresponding removal from the metal has already occurred.

A natural answer may be that a suitable time allowance should be

made for this lagging of the metal behind the slag in its loss of iron oxide, and that a fuller removal of this oxide from the slag should be required when, in coke practice, the removal is initiated in the slag than in the American practice in which it is initiated in the metal.

To be accurate, even in coke practice, while the coke is initiating this removal in the slag, the carbon of the metal is also carrying it on there.

35. *Summary of Advantages and Disadvantages.*—We aim rather to expose than impose practice. Now that we have seen the advantages and disadvantages of these two practices, the oring and the oreless, we may well remember that excellent as the results of our American fine-steel practice are, it has evolved under the American high-pig traditions, and that there has been no fair chance to compare exhaustively and conclusively the features in which those two practices differ. This is as true of the temperature differences as of those of oring. Such a comparison should be to the interest of all concerned, the public included. Each operator will reach the best results with the practice to which he is accustomed, but this does not indicate that he might not get still better results with some modification of his practice, once he is well accustomed to it.

The following numbers may serve as a nucleus for the data needed for such a comparison as we have just referred to. The physical properties called for in the first line are those required by the specifications of the United States Government for gun steel, whereas, if we are advised correctly, those of the second line are specified by some foreign governments.

AMERICAN AND ONE FOREIGN SPECIFICATION FOR CANNON STEEL

	Tensile Strength, Lb. per Sq. In.	Elastic Limit, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Contraction of Area, Per Cent.
American	95,000	65,000	13	30
Foreign	92,000	57,000	14	not specified

We further understand that where an elastic limit as low as 52,800 lb. to the square inch is accepted, provided the contraction of area is at least 26.4 per cent., the foreign practice also makes use of the impact test, but we believe that the test prescribed would not in fact reject any metal which passes the American specifications. Recently wide experimentation has been made in impact tests in addition to the foregoing, and much new light has been obtained.

TEEMING, MOLDS, ETC.

36. *The Ladle.*—A good deal of metal rich in inclusions is likely to accumulate on the very bottom of the ladle and particularly about the stopper, because the relatively cool ladle bottom cools the steel first tapped upon it, and thus thickens it, and impedes the rising of the inclusions which it contains. Therefore, the first 300 or 400 lb. of steel which run through on raising the stopper should be poured into an old mold set

up beside the regular ones, and should be treated as scrap. The ladle should then be brought over the regular molds, but in doing this at so early a stage before the stopper and nozzle have become highly heated, care should be taken not to close the stopper tightly lest it should stick in the pasty metal when we try to reopen it.

37. *Temperature and Rate of Pouring.*—(*a*) These need to be governed accurately so as to steer between two grave dangers, that of causing external cracks in the ingot from too hot or too fast pouring; and that of causing external roughness and of increasing the quantity of inclusions by too cold pouring.

(*b*) As the first part of the liquid steel is poured into its mold, its outer layer which is in immediate contact with the cold iron walls of the mold cools down quickly through the transfer of its heat to those walls, with the consequence that a thin crust of solid steel soon forms on the outside of the mass, and thickens progressively. As it thickens the pouring of the steel continues, so that the top of the column of steel in the mold rises continuously. Thus as the crust of solid steel encasing the still liquid interior of the ingot progressively thickens, it is exposed to a continuously increasing hydrostatic, or ferrostatic, pressure.

This increase may be so rapid that the hydrostatic pressure outstrips the increasing strength of the solid crust of the ingot, and thus bursts it, forming one or more external cracks. These form all the more readily because at this stage the mold itself is rapidly growing hotter, and therefore expanding and drawing away from the ingot crust, the outer layers of which are cooling and hence contracting.

Both hot pouring and fast pouring increase the tendency of the hydrostatic pressure to outstrip the strength of the crust, and thus to crack it—hot pouring because it retards the thickening of the crust, and fast pouring because it accelerates the increase of the hydrostatic pressure. This is one of the most important reasons for the American practice of cold pouring, the other reason being that it gives quick solidification and shortens the pipe.

This race between thickening and strengthening of the crust on one hand, and the hydrostatic pressure on the other is illustrated by Fig. 2, which shows a series of paraffin ingots poured at different rates and emptied as soon as they were poured full. Note that the thickness of the walls, and especially of the lower part of the walls, at the moment when the mold is thus filled completely, increases greatly from left to right, with the length of time occupied in pouring. Thus in ingot 5, poured in 10 min., the walls have reached a fair thickness. In ingots 7 and 8, poured still more slowly, this thickness is still greater.

Here cool pouring is the equivalent of slow pouring. Each favors the thickening of the solid crust relatively to the lengthening of the column of molten steel, and each thus guards against external cracking.

This leads to the simple rule that the steel should be poured at so low a temperature and so slowly that the solid walls at the lower part of the ingot will thicken fast enough to resist the progressively increasing hydrostatic pressure caused by the gradual rise of the upper surface of the metal.

An additional and closely related effect of the slow pouring is to shorten the pipe. This is because the steel cools more slowly in the ladle

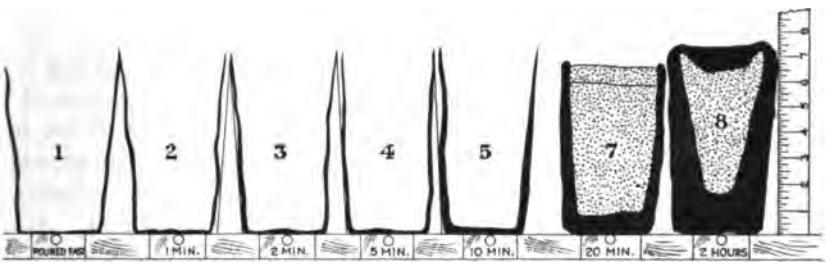


FIG. 2.—PROGRESSIVE THICKENING OF WALLS OF PARAFFIN INGOT AND INCREASE OF TAPER, AT MOMENT WHEN MOLD IS COMPLETELY FILLED, WITH TIME OCCUPIED IN POURING. MOLD EMPTIED AS SOON AS FULL.

than in the molds, so that slow pouring prolongs the period during which we add fresh hot steel to the ingot top, while the lower part of the ingot is cooling by transferring heat into the mold walls. In general, slow pouring makes for keeping the ingot top hot.

(*c*) A further objection to hot pouring is that to raise the temperature of the molten steel is to raise the temperature to which it heats the mold walls at any given instant, hence to retard the cooling of the steel, and

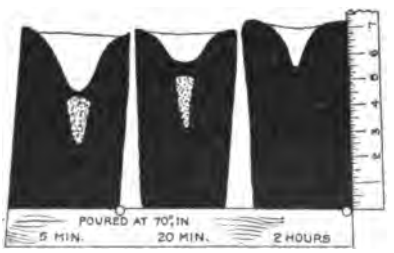


FIG. 2*a*.—SLOW POURING SHORTENS AND RAISES THE PIPE. (PARAFFIN INGOTS ALLOWED TO SOLIDIFY COMPLETELY.)

in particular to retard its passage through the solidification range. In this way hot pouring leads to a greater degree of differentiation in solidifying, to the formation of larger dendrites, and to a higher degree of enrichment by segregation in the interdendritic spaces and probably in the axial region. The crucible steel maker long ago noticed the marked columnar structure of ingots poured too hot, and called those with this structure "scorched."

38. *Cool Pouring.*—(*a*) If, on the other hand, the steel is too cold when it is poured, or is poured so slowly that it becomes too cold before the whole of it has entered the mold, two serious troubles arise. First, the extremely slow rising of the upper surface of the molten metal in contact with the cold mold easily causes the surface to crust over momentarily for a short distance, somewhat as sketched in Fig. 3. These slight crustings may not be entirely effaced by the metal poured in later if the steel is extremely cold.

(*b*) Another and still more serious damage by too cold pouring is the retention of inclusions. Steel poured so cool that the thickness of the solid walls of steel gradually forming in the mold increases fast enough to resist the progressively increasing hydrostatic pressure, must evidently be very near its solidus as it enters the mold. At any rate, it must be well below its liquidus, and therefore it must be an emulsion of particles of solid steel supported in molten steel. This point must be grasped clearly. The lower the temperature is the greater will be the proportion of solid particles to molten steel; and the more viscous therefore will be the emulsion of which the steel itself consists. Evidently this viscosity impedes the attempt of the particles of slag to rise to the surface.

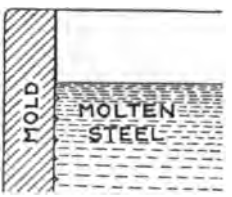


FIG. 3.—SIDE ROUGHNESS DUE TO TOO COOL OR TOO SLOW TEEMING.

(*c*) Another danger in the top pouring of ingots at too low a temperature is that, should the nozzle leak, so that its spittings form a thin sheet which solidifies on the side of the mold above the level of the steel, the metal poured later may not be hot enough to remelt this sheet, which thus remains to form a discontinuity. As it melts at its bottom, it may fall down into the molten metal below, or tilt over and catch on the opposite side of the mold. Evidences of this have frequently been observed and thoroughly traced to this cause.

39. *Summary.*—To sum up the three advantages of cool pouring which we have now seen, that it restrains segregation probably both axial and interdendritic, the size of the dendrites, and the tendency to external cracking, outweigh its disadvantage of favoring the retention of inclusions in the opinion of American open-hearth experts, but not in that of Continental European ones and at least some of the British, who purposely pour their gun steel extremely hot. Indeed, even their workmen regard the external cracking to which hot pouring leads as a favorable symptom, for the cracks can be chipped out while the greater freedom from inclusions persists. In our opinion the question is an open one, to be decided by careful observation. Yet because our paper is to describe American practice, we shall continue to speak of cool pouring as among the aims of the process.

Cool pouring is considered further in Section 47.

40. *Notes on Pouring.*—(*a*) The interval between tapping and teeming and the rapidity of teeming are governed by the melter's judgment as to the temperature at which the steel left in the furnace, and by the size and number of ingots into which the charge in the ladle is to be poured. The length of time occupied in teeming each ingot should be recorded carefully for the melter's guidance in future cases. If the ingots show external cracks, referable to too hot pouring, he would infer that he had poured too fast for the actual temperature of the steel. If, on the other hand, the ingots show the characteristics which we associate with too cool and hence too slow pouring, such as an excessive quantity of inclusions, he infers that for the existing conditions he has teemed too slowly. Laps and cold shuts on the corners of the ingot are clear evidence of too slow pouring.

(*b*) Each heat of steel, and each ingot of each heat, forms in itself a problem for the melter, whose judgment and experience are now called into operation, since it is well nigh impossible fully to lay down rules governing the pouring. In all cases the melter, who should be the most experienced man available in the establishment, should himself watch the steel in each ingot as it is rising in the mold, and judge the temperature of the metal and the speed of pouring required for each, carefully recording the actual time and the conditions of the resultant ingot. The proper rate of pouring cannot be predetermined; rather it is estimated by the melter, with his experience in mind, from the observed temperature of the steel as it rises in the mold.

(*c*) It is obvious that top-poured ingots are difficult to watch in the way just mentioned. This matter will be discussed more fully when top and bottom pouring are considered (Section 55).

(*d*) The temperature of the steel in the ladle falls continuously from the beginning to the end of teeming, with the effect that though the metal was slightly above its liquidus on entering the ladle, it falls to materially below it before the teeming is completed, so that some skull often remains. This skull represents metal too pasty, and hence too near the solidus, to flow over the bottom of the ladle. Its presence is a sign that the temperature and rate of teeming have been correct.

41. *Breaking Cream.*—It is a common saying that the appearance of bottom-poured steel as it rises in the mold should be that of "breaking cream." This is readily understood when we remember that the metal poured at the proper temperature is an emulsion much like that of the suspended butter fat of thick cream. Both are subject to crusting over with a very thin crust. In the case of steel, this crust caused by the cooling effect of the air in the neighborhood of the mold is quickly remelted by the hot steel rising from below, if the pouring temperature is proper.

42. *Stop-pours.*—(*a*) We should pour the steel into each mold without the slightest interruption, lest we form a "stop-pour," a slight freezing of

the upper surface of the metal where it touches the mold, and fail to remelt it completely when we resume the pouring. This is especially important in the cool pouring recommended in this paper.

(*b*) Stop-pours may be made both in bottom-pouring and in top-pouring practice, and sometimes are difficult to detect, especially if the stoppage is very short. In any event, when a stoppage has occurred and the resultant stop-pour has escaped detection, it is likely to be discovered if the ingot is forged, but if the ingot is rolled discovery is much more difficult. Always after a stoppage there is certain to be a defect in the surface, extending to unknown depths into the section. For gun purposes, and others in which the ends only can be inspected and tested, a stop-poured ingot never should be considered for use. There are, of course, occasions when for bar steel or billet production, a stop-poured ingot can be carried forward and the stop-poured part cut out and discarded.

43. *Piping.*—(*a*) The reasons for the existence of the pipe are already familiar, namely, that at an early stage in the solidification the crust of the ingot has done a greater proportion of its total cooling, and hence of its total contraction, than has occurred in the deeper seated layers, and thus has been stretched by their resistance. Because these deeper seated layers therefore have from this time on a greater range of temperature to cool through than the crust has, they will undergo more contraction than it. This excess of contraction of the interior plus the stretching of the crust are represented by the presence of an axial cavity, or pipe, unless indeed it is compensated for by the formation of blow-holes or gas cavities.

(*b*) One of us[6] has already shown that the pipe forms in the last solidifying part of the ingot, whether that is at the top or bottom or at the side. Clearly it is well to have the pipe occur at one end of the ingot so as to affect only a short part of its length, and that end is preferably the top for obvious reasons.

Hence the various devices for concentrating the heat at the ingot top, or otherwise causing the solidifying of the top to lag behind that of the parts below, so that, as fast as the pipe tends to form, it may be filled by still molten metal from above. Among these devices, are "hot-tops" to the molds, sink heads, having the large end of the ingots uppermost, pouring slowly, at a low temperature, and at the top of the ingot especially at the last, and of making the mold walls thicker below than above, so that they may cool the bottom of the ingot faster than the top. This will be considered further in Section 55, on top and bottom pouring.

44. *Top lag*, or the lagging of the upper part of the ingot in the process of cooling, may here be studied a little more closely because it helps

[6] H. M. Howe and Bradley Stoughton: *Trans.* (1907) **38**, 117.

explain why small ingots are nearly always top poured throughout, though larger ones are not (Section 55).

In any given transverse slice EE', Fig. 4, of a solidifying ingot, the temperature rises continuously as we pass from the outside toward the axis, while it simultaneously rises continuously as we pass from this slice upwards. The tendency to form an axial cavity or pipe proves that, while this tendency exists, the slice EE' as a whole is contracting faster than the crust of the ingot. The parts E and E' are held apart by the rigidity of the crust, and the excess of contraction of the crust gives the different parts of the slice a tendency to draw apart, as sketched by the arrows A and B. This tendency, unless restrained, causes the pipe D.

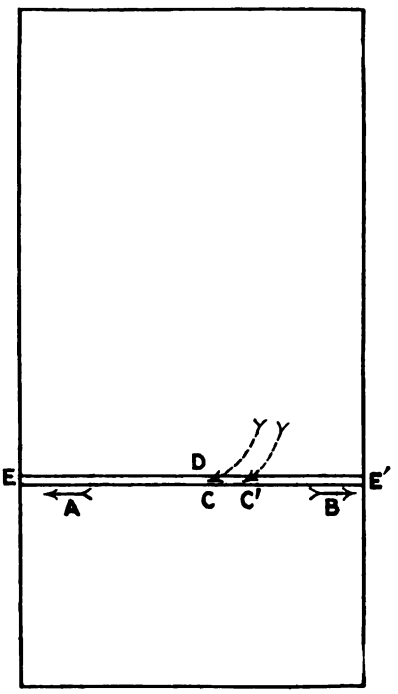


FIG. 4.—PIPE FORMING AND PIPE CLOSING TENDENCIES.

Lest it be thought that this tendency to crack open at the axis is confined to the temperature range between the liquidus and the solidus, a range indeed of great weakness, let us remember that pure substances, pure metals, pure eutectic liquids, etc., in which the solidus and the liquidus coincide and there is no freezing range but only a true freezing point, also pipe. Indeed this case is not needed to convince us that the slice EE' may crack at its axis and may thus tend to start a pipe at any temperature at which the stretch AB caused by the resistance of the rigid ingot crust to the contraction of the slice because of its faster cooling, exceeds the stretching power of the metal; or in other words, when the stress so induced exceeds the existing strength of the metal. This range of temperature may extend far below the solidus.

45. *Pipe-closing Period.*—Imagine that the slice EE' is completely isolated from the mass of metal above and below by the planes which form its top and bottom. In this case the pipe D, representing the excess of induced stretch over capacity for stretch, persists. But if, having thus imagined the creation of D, we next consider the actual conditions in which no such planes exist, we see that all of the metal above this plane which is still hot enough to have any appreciable capacity for flow, begins sagging down to close D, as suggested by arrows C and C', quite as the faces of a prism of soft jelly sag when the mold in which it has set is with-

drawn. The curved lines of flow of such concrete masses are not to be confused with the angle of repose of discrete ones like sand. Note that the sides of the funnel-shaped part of any pipe are curved and not straight.

Thus in every imaginary horizontal layer there is the pipe-forming tendency, representing the excess of induced stretch over capacity for stretch, and the pipe-closing tendency, representing the sagging of the overlying mass, and chiefly of its axial and periaxial parts, which are the hottest and hence the most mobile.

The pipe will stretch down to the layer in which the sagging of the overlying mass just fails to compensate fully for the pipe-forming tendency. Clearly the quantity of sagging down into any given layer must increase with the volume of mobile metal above the layer, and with its mobility, and this latter in turn increases with the steepness of the vertical thermal gradient from this layer up. In other words, in any given horizontal layer, the pipe-closing tendency increases with the mobility and hence with the temperature of the metal above, and these increase with the rapidity of rise of temperature from this layer up. Hence the importance of concentrating the heat at the top of the ingot, thus increasing the volume and mobility of the metal available for sagging down into any given layer, thus raising the position of the layer the sagging into which barely equals in volume the volume which the pipe-forming tendency represents, and thus in fine shortening the pipe.

Because the tendency to pipe is inversely as the steepness of the vertical thermal gradient in the upper part of the ingot, and because this steepness is inversely as the size of the ingot, other things being equal, the tendency to pipe and the depth of the pipe are greater in small than in large ingots. This result represents also the longer time available in large ingots for the sluggish process of sagging.

46. *Stub Ingot Pouring.*—In making "stub"[7] tire ingots, that is, those the length of which is only 60 to 100 per cent. of their diameter, each making a single tire, the Standard Steel Works Co. combines various steps for causing the cooling of the ingot top to lag and thereby shortening and raising the pipe, and raising and concentrating the segregate so effectively that a discard of only 3 per cent. suffices to remove all unsound, piped, and harmfully segregated metal. This discard is the small disk punched out of the axis of the bloom into which the ingot is forged in working it into the shape of a tire.

Here the cooling of the bottom is hastened by the broad, thin, cheese shape of the ingot which exposes entended bottom surface to the cold thick bottom of the mold; and the cooling of the top is retarded by a layer of carbonaceous matter, which in burning yields much heat yet without causing material carburization.

[7] Lawford H. Fry: *Year Book* Amer. Iron and Steel Inst. (1919) 435.

47. *Cool Pouring Raises the Pipe.*—Section 37 shows that in top pouring we may raise the pipe by pouring slowly. Cool pouring has a like effect, as we will now explain. First, let us recognize that the molten steel cools down much more slowly in the ladle than in the molds. With this in mind the effect of cool pouring in raising or even eliminating the pipe can be made clear by considering two imaginary extreme cases.

First let us suppose that the steel when top poured into the mold is so extremely cool that it solidifies very rapidly, indeed almost immediately. In this case, the early poured steel solidifies very early in the pouring, and is thus anchored in place at the bottom of the mold. Each subsequent addition in like manner becomes anchored approximately at the height in the mold which it occupied when poured. These successive lots thus cool down by the transfer of their heat into and through the mold walls. Because the first poured lot starts this cooling earlier than the later ones, it will at any given instant be the coolest, and each of the successive lots, from the bottom upwards, will be hotter at any given instant than the one next below it. Thus solidification and the formation of the pipe proceed from below upwards, so that each layer, as it enters the mold, finds the pipe already formed or forming in that beneath it, and thus has the best possible opportunity to fill it. Indeed this, like any other means of causing the solidification of the top to lag behind that of the lower parts, clearly tends to raise the pipe.

In bottom pouring the same is true, save that here we must conceive that the steel is at all times hot enough to keep a channel open through the earliest poured and earliest frozen layers at the bottom.

Turning now to the opposite extreme, let us suppose that the steel is so hot that none of it freezes before the whole ingot is poured. In this case the falling or rising stream keeps the whole mass in motion, so that the parts poured first become mixed with the rest, and that the progressive rise of temperature from the bottom upwards, so favorable to the raising and shortening of the pipe, is reduced to a minimum.

The principle which governs these two extreme cases applies to any intermediate one. The cooler the steel the more of the early poured parts will solidify and become anchored in the lower part of the mold, and the more rapid will be the rise of temperature at any given instant from the bottom toward the top, and hence the shorter and higher up will be the pipe.

48. *Shape of Molds.*—In designing the molds there are four important ends to be sought:

(*a*) That they shall have enough taper to prevent the ingots from sticking to them, but no more.

(*b*) That the crust of the ingot shall not be cracked transversely by its inevitably cooling and contracting faster than the deeper seated layers.

(*c*) That it shall not be cracked longitudinally by the same cause.

(*d*) That the pipe shall be shortened and raised as far as possible, or better still eliminated.

Let us consider the means to certain of these ends.

49. *Taper.*—(*a*) Fig. 5 shows the taper of ingots of five sizes, taken from current good practice. The taper is almost the same in all of these, varying from 0.40 to 0.43 in. in diameter to the running foot (see Table 1).

(*b*) On pouring the ingot into its mold, its skin solidifies when its temperature is much above that of the mold so that the ingot in cooling has a greater range of temperature through which to cool than the mold, and hence contracts more. This excess of contraction of the ingot would naturally cause a gap between them, so that it might be expected that, were both perfectly smooth, no taper would be needed. In fact, neither is quite smooth. The ingot especially is likely to have roughnesses which may cause it to stick in the mold. Moreover, part at least of the gap to be expected between ingot and mold is effaced by the stretching of the ingot's crust caused by the resistance to its contraction by the slower cooling and contracting deeper seated layers, as well as by the stretching due to ferrostatic pressure.

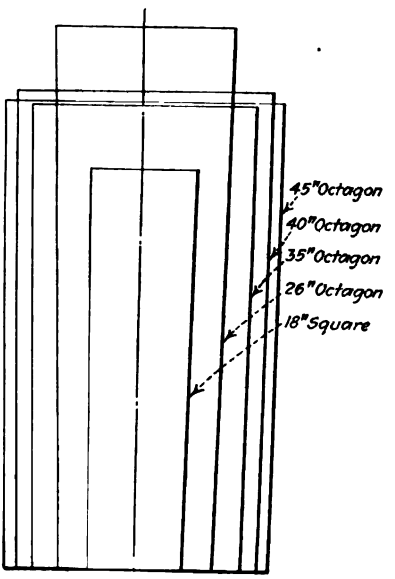


FIG. 5.—TAPER OF INGOTS.

(*c*) It is to afford the clearance needed for easy stripping that the taper is given.

(*d*) The amount of taper should be the minimum which experience shows is needed to enable carefully poured ingots to be removed from carefully prepared molds, because any great excess of taper makes the work of forging more difficult, and also leads to the faster heating of the smaller than of the larger end of the ingot.

(*e*) Further to prevent this sticking, the inner surface of the mold should be examined carefully to detect any roughness, and it should be coated, for instance with a wash of bone graphite and water, and polished to a "kitchen range" surface.

(*f*) It might at first be thought that more taper would be needed in small than in large ingots, because the average temperature of a large ingot at the time when its crust is solidified by being cooled by the mold and its external dimensions are thus determined, is higher than that of a

small ingot. This suggests that the average contraction of a large ingot is greater than that of a smaller one. Because this excess of contraction helps to free the ingot from the mold, less taper would naturally be needed to give enough free space to enable the ingot to slip past the mold.

(*g*) But this advantage of the larger ingot is counteracted by its disadvantage as regards the stretching of its crust by the resistance of the slower cooling deeper seated layers. Both large and small ingots are stripped as soon as they have cooled far enough to be handled without danger of breaking, when the faces of the octagon or square are at about 850° C. (1562° F.), and the edges or corners are black, and these temperatures are about the same for large as for small ingots. But the average temperature of the large ingot at this time is much higher than that of the small one. Hence, the resistance of the slower cooling interior of the large ingot stretches its crust by an amount greater than the corresponding stretching of the crust of the small ingot. This greater stretching of the crust of the larger ingot lessens the clearance between ingot and mold, and this offsets to a certain degree, and perhaps completely, the excess of contraction of the large ingot to be expected from the considerations set forth in the preceding paragraph.

50. *Prevention of Longitudinal Cracks by Giving the Crust of the Ingot an Accommodating Shape.*—(*a*) A circular gutter pipe filled with water bursts on freezing, because the circular form of the metal has too little power of elongation to accommodate itself to the expansion of the freezing water. But a corrugated gutter pipe does not burst, because while its metal has no more capacity for elongation than that of the circular one, it has an accommodating shape.

(*b*) Following this line of reasoning, the crust of the ingot is given a similar accommodating shape, often that of a fluted octagon, in order that it may not be torn apart by longitudinal cracks in the early stage of solidification, when it is thin and tender, by the resistance to its contraction offered by the slower cooling of the deeper seated layers; but that instead it may bend and thus accommodate itself to the resistance.

51. *Prevention of Transverse Cracks by Giving the Crust of the Ingot Firm Salient Ties.*—(*a*) The ingot may be torn transversely, not only by the resistance of the slower cooling, deeper seated layers to its longitudinal contraction, but also by any other impediment to that contraction, for instance by its being caught at its top by a fin, or by some roughness in the mold. In this case the weight of the part of the ingot below the obstruction may suffice to cause transverse cracks, especially because its effect is always aggravated by the resistance of the slower cooling, deeper seated layers to the faster longitudinal contraction of the skin. Mechanical attachment of the upper part of the ingot to the mold is more likely to occur when the large end of the ingot is uppermost. The obstruction to

longitudinal contraction is, of course, all the worse if the ingot is caught at both ends by the mold.

(*b*) In order to prevent this transverse cracking by excessive longitudinal stress, the ingot should be provided with saliences which, by outrunning the cooling of the non-salient parts, become in fact more or less firm ties. The four main edges of a square ingot are such saliences, which thus become longitudinal ties, and by their integral union with the metal of the faces of the square tend to prevent it from being torn transversely by the longitudinal stress.

52. *Octagonal and Square Molds.*—(*a*) The chief advantage of an octagon is that it has twice as many of these supporting edges to act as longitudinal ties, and prevent the faces between from being torn across by any resistance to the longitudinal contraction of the ingot.

(*b*) It might at first be thought that, if increasing the number of faces from four in a square to eight in an octagon is an advantage, we should get a further advantage by still further increasing them to twelve or even more. In some works ingots with as many as twelve edges are made. But if we push this too far we fail to accomplish what we seek. If the number of edges were infinite, the ingot would be a cylinder. It would in the first place have the most unaccommodating shape possible, and in the second place would have no ties for preventing the cracking of the faces. The more edges there are, the less can each edge project beyond the faces between which it lies, without running the risk of cracking in cooling, and of folding in forging, and the less therefore can it outrun the cooling of the faces and the less support can it give them.

TABLE 1.—*Dimensions of Ingot Molds Shown in Figs.* 7 *and* 8

Nominal Size	18 In. Sq.	26 In. Oct.	35 In. Oct.	40 In. Oct.	45 In. Oct.
Radii, in inches:					
of edges		1.50	1.50	1.50	1.25
of fluting		14.875	20.00	20.00	28.00
Taper, inches, of diameter per foot of height	0.3985	0.4220	0.4232	0.4305	0.4148
Height, inches	60.25	87.312	76.062	78.375	76.75
Ratio height to nominal diameter	3.35:1	3.36:1	2.17:1	1.96:1	1.71:1
Ratio, thickness of ingot to thickness of wall at top	5.38:1	4.29:1	4.12:1	4.46:1	4.57:1
At bottom	2.30:1	2.63:1	3.17:1	3.18:1	3.81:1

(*c*) The purpose of making the faces of the octagon concave is to give its eight edges greater salience, so as to increase the degree to which they outrun the cooling of the faces between them, and thus to increase the support which they offer them.

(*d*) The square has the further disadvantage when compared with the octagon that its corners in cooling tend to outrun the intermediate faces so greatly that a sort of St. Andrew's cross, or plane of weakness running diagonally from corner to corner of the square, forms readily. It is the junction of columnar crystals starting out from the adjoining faces, somewhat as sketched in Fig. 6.

This tendency should be lessened, first by making the mold much thinner at the corners than at the faces of the square, as is shown in Fig. 6, and second by rounding the corners. Yet this rounding should leave them as sharp as is compatible with their not crusting during pouring, and with their not forming these diagonal planes of weakness, because to dull them brings the periphery toward the cylindrical form, and thus lessens its power of accommodating itself to the resistance of the slower cooling interior. In general, the radius of the faces is about half the diameter of the ingot.

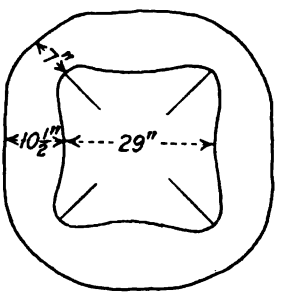


FIG. 6.—ROUNDING AND THINNING THE EDGE OF A SQUARE MOLD.

Square ingots may well have concave sides between the corners of the square, if they are to be bloomed, so that they may ride more easily, and be the more easily guided, on the feeding table of the blooming mill; whereas they are frequently made convex when the ingot is to be forged. In an octagonal ingot, the faces should have the shortest radius, and the edges the greatest salience, that will not lead to the formation of folds in forging.

(*e*) An additional reason for not making the vertical edges of either the square or the octagonal mold too strongly salient, is that the salience, if too strong, would outrun the rest of the ingot in heating for forging so greatly as to be in danger of being burned. There are other limiting considerations which could be discussed, were it not for burdening this paper with too much detail.

53. *Examples of Molds.*—Table 1 and Figs. 7 and 8 give the dimensions of ingot molds of five different sizes from very good practice. The molds would probably be improved by thinning their walls at the top and thickening them at the base as shown in Fig. 8, which gives the dimensions of the molds at another well managed establishment. This tapering of the mold walls has been carried out successfully ever since 1897 in making fine steels.

One steel maker advises that, for ingots about 24 in. in diameter, the ratio of the cross-section of the mold to that of the ingot should be two to one at the bottom and a little more than one to two at the top, though this may make the mold too fragile at the top for rough work. On the other hand for ingots more than 24 in. in diameter,

the two to one ratio would give the bottom of the mold a clumsiness that would hardly be compensated for by the extra heat which it would absorb from the ingot bottom. Hence this ratio should decrease as the diameter of the ingot increases beyond 24 inches.

54. *Hot Top and Discard.*—(*a*) The ratio of the steel in the hot top to that in the ingot proper should, in general, be from 15 to 25 per cent., according to the specifications as to top discard. For instance, for gun steels the Government requires 30 per cent. top discard. It is convenient and wise to let 25 of this 30 per cent. be made up by the steel con-

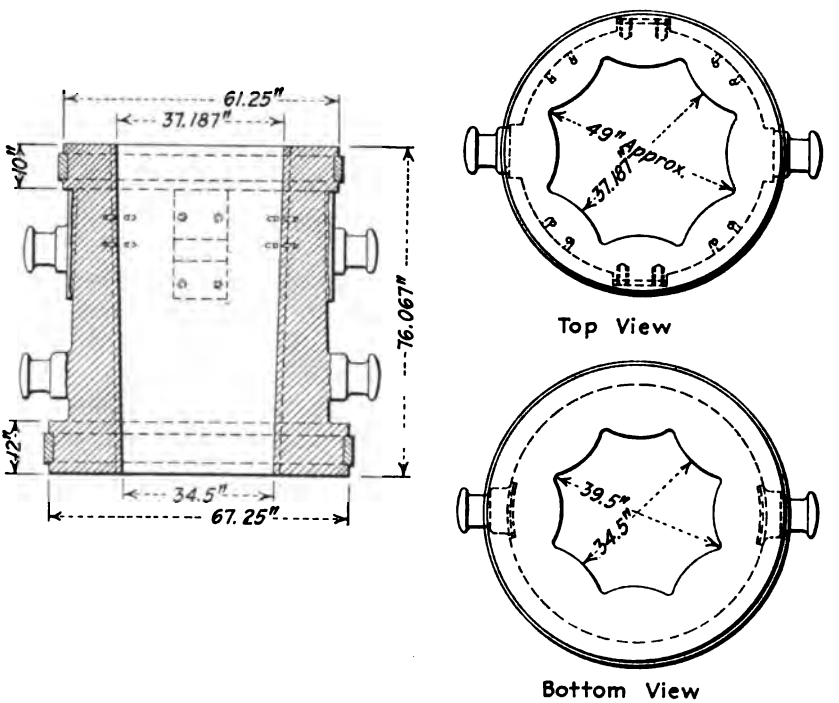
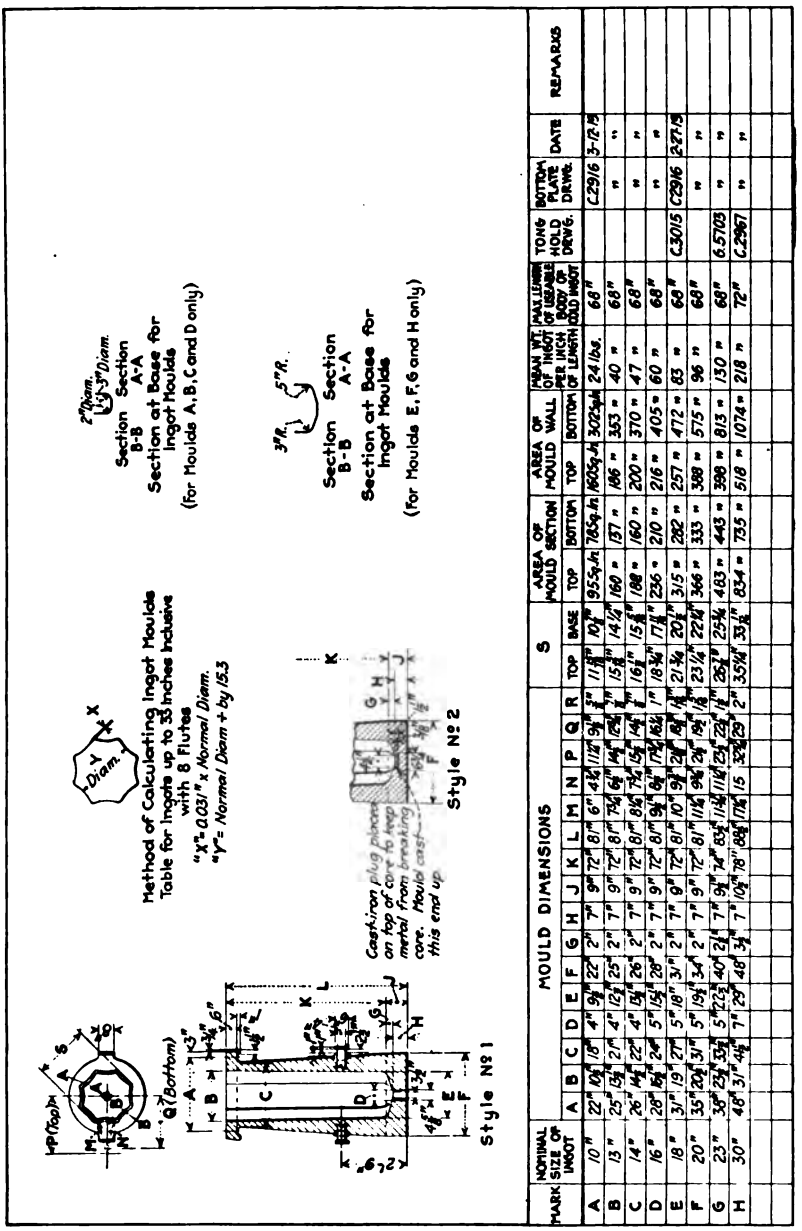


FIG. 7.—CHILL MOLD FOR 35-IN. OCTAGON INGOT.

tained in a sand-lined sink head, and the remaining 5 per cent. by the few inches of the top of the ingot proper which could not be used for gun steel in any event, because they form the joint between the ingot and the skin head.

(*b*) The purpose of the discard is to remove any mechanically unsound parts, and any that are unduly enriched in phosphorus and sulfur by segregation. With the use of a hot top, and with well-made steel carefully poured, there is much less than 30 per cent. of the ingot that is subject to mechanical unsoundness. Moreover with well-made, thoroughly deoxidized steels very free from phosphorus and sulfur, such as can be

made in the electric furnace, the content of phosphorus and of sulfur cannot become harmfully great even at the local enrichment at the ingot top.



MARK	NOMINAL SIZE OF INGOT	MOULD DIMENSIONS A	B	C	D	E	F	G	H	J	K	L	M	N	P	Q	R	S TOP	S BASE	AREA OF MOULD SECTION TOP	AREA OF MOULD SECTION BOTTOM	AREA OF MOULD WALL TOP	AREA OF MOULD WALL BOTTOM	MEAN WT. OF INGOT PER INCH OF LENGTH	MAX. LENGTH OF USABLE BODY OF COLD INGOT	TONG HOLD DRWG.	BOTTOM PLATE DRWG.	DATE	REMARKS
A	10"	22"	10¼"	18"	4"	9¼"	22"	2"	7"	9"	72"	8"	6"	4¼"	1 1/2"	9¼"	5"	11⅞"	10⅞"	955 sq.in.	765 sq.in.	1605 sq.in.	1302 sq.in.	24 lbs.	68"		C2916	3-12-15	
B	13"	25"	13¼"	21"	4"	12"	25"	2"	7"	9"	72"	8"	7¼"	4¼"	1 3/4"	12¼"	6"	14⅞"	13⅞"	1160 "	937 "	1936 "	1577 "	40 "	68"		"	"	
C	14"	26"	14"	22"	4"	13¼"	26"	2"	7"	9"	72"	8"	8¼"	5¼"	2"	13¼"	6"	16"	15⅛"	1288 "	1060 "	2200 "	1810 "	47 "	68"		"	"	
D	16"	28"	15¼"	24"	5"	15¼"	28"	2"	7"	9"	72"	8"	9¼"	6¼"	2"	15¼"	6"	17⅛"	17¼"	1536 "	1260 "	2616 "	2150 "	60 "	68"		"	"	
E	18"	31"	19"	27"	5"	18"	31"	2"	7"	9"	72"	8"	10"	9¼"	2"	18"	6"	21⅛"	20¼"	2015 "	1652 "	3432 "	2820 "	83 "	68"	C3015	C2916	2-27-15	
F	20"	35"	20"	31"	5"	19¼"	34"	2"	7"	9"	72"	8"	11¼"	9¼"	2"	19¼"	6"	23⅛"	22¼"	2566 "	2100 "	4368 "	3590 "	96 "	68"		"	"	
G	23"	38"	23"	33"	5"	22"	40"	2"	7"	9"	74"	8"	13"	9¼"	2"	22"	6"	26⅛"	25¼"	3217 "	2640 "	5472 "	4500 "	130 "	68"	6.5703	"	"	
H	30"	48"	31"	44"	7"	29"	48"	3"	7"	10"	78"	8"	17"	13"	2"	29"	6"	35⅛"	33⅛"	4834 "	3975 "	8232 "	6770 "	218 "	72"	C.2967	"	"	

FIG. 8.—DIMENSIONS OF MOLDS THICKENED AT BASE AND THINNED AT TOP.

Hence it is expected that this 30 per cent. top discard will be reduced to 20 per cent., or even less in special cases. This would be wholly justified.

(*c*) The use of sink heads of sand in top pouring is open to the objection that the stream of very hot steel, running down in the neighborhood of the sand, is apt to heat it so suddenly and so highly that it disintegrates, so that enough of it runs down into the mold to add appreciably to the inclusions.

(*d*) The use of carbonaceous material in the sink head implies a certain danger that the carbon may be taken up by the upper layers of steel, and may be carried down to a very considerable depth, partly by diffusion and partly by convection. Sulfur prints of ingots have shown clearly, what was indeed evident on careful consideration, that there is a very great degree of sagging down or sinking down along the axis of the ingot.

55. *Top and Bottom Pouring.*—Bottom pouring has the advantages:

(*a*) That in it the upper surface of the molten metal is visible throughout the operation, for the guidance of the pourer, whereas during the early part of top pouring from a bottom-poured ladle the ladle itself cuts off our view of the surface of the ingot. This disadvantage of top pouring may sometimes be avoided by pouring from a lip, or through a head box.

(*b*) That the surface is not disturbed, as in top pouring, by the impact of a falling stream of metal, and hence that its indications are more decisive, more easily interpreted.

Both these advantages are of less weight for very wide ingots than for those of intermediate size, because the surface of the former becomes fully visible earlier, and is less disturbed by a descending top-poured stream than that of the latter.

(*c*) That it permits group pouring, leading to great uniformity of conditions among the ingots of a given lot.

(*d*) That during all but the latter part of the pouring, the rapid uprush of the stream along the axis of the mass tends to lessen the quantity of heat which it transfers to the lower part of the ingot, and to increase correspondingly that which it gives to the ingot top, thus lessening the tendency to pipe. This effect of bottom pouring is favored by the shape which the inner surface of the walls of the ingot assumes, that of an inverted cone. This merit of bottom pouring increases with the velocity of the uprising stream, and hence increases with the size of the ingot, and decreases as the pouring progresses.

(*e*) That it avoids cutting the bottom of the mold by the impact of the falling stream of metal, as occurs in top pouring of long ingots.

On the other hand bottom pouring is at a disadvantage:

(*f*) In needing more complicated molds, more expensive to place.

(*g*) In scrapping some of the metal in the form of runners, etc.

(*h*) In its liability to befoul the steel with matter cut or fluxed from the runner bricks.

(*i*) In increasing the danger of "run-outs" by its keeping the metal in the runners molten.

(*j*) In giving up to the bottom of the ingot an undue proportion of the heat of the last of the fresh hot steel added, thus increasing the tendency to pipe. This is because, during the last of the pouring, the rise of the incoming steel along the axis of the ingot is necessarily slow, both because now the level of the steel in the mold can be but little below that in the runner, and because the steel must now be added cautiously and hence slowly in order that the ingot may be given the predetermined height accurately. In top pouring, on the other hand, the last of the hot steel is added directly and slowly to the top of the ingot to which most of its heat is transferred, very little reaching the lower part of the mass.

This advantage of top pouring probably outweighs the corresponding advantage (*d*) of bottom pouring, both because the upward concentration of heat by (*d*) does not apply to the uppermost part of the ingot, the part which has the greatest effect on the piping tendency, and because this concentration occurring early in the pouring, is undone more or less by the equalizing processes of convection and diffusion. Here let us review considerations (*a*) and (*h*).

(*a*) Though bottom pouring requires more apparatus, more equipment, and more time for setting up the equipment in the open-hearth department, than is usual for top pouring, it has the greatest outstanding advantage that each individual ingot can be watched during its making, and the speed of the incoming stream of metal adjusted in exact conformity with the requirements of the temperature and composition of the metal and the size and shape of the mold. These and all the other factors governing the production of a successful ingot are found to be under much more thorough observation and control in bottom pouring than has as yet been possible in top pouring.

(*h*) As to the introduction of inclusions through fluxing bricks comprising the runner, this is, of course, possible. But if the requisite degree of care is given to the selection of the brickmaker, the material from which the bricks are made, the nature of the burning of the bricks, and the care with which they are fitted together and the joints protected, it will be found that there is only a negligible amount of inclusions due to fluxing of the inner surface of the bricks by the stream of metal entering the molds. This is obviously true, because the time occupied by the metal passing through these bricks is too short for anything but the immediate surface of the brick to become heated to the point where it will flux to a dangerous degree. A far greater source of danger of inclusions from the introduction of foreign material is chargeable to the molten inner lining of the ladle, especially near the nozzle where the metal rushes with greatly increasing velocity through the narrow aperture afforded by raising the stopper, and, immediately around the nozzle, scours across a considerable area of ladle bottom where it and the ladle lining have been at a high temperature for a comparatively long time.

These considerations explain the course actually followed. Little crucible ingots, weighing about 90 lb. each, and small ingots in general are top poured; larger ones from 9 to 55 in. in diameter and weighing from 1000 to perhaps 150,000 lb. are general by bottom poured; while very large ones, for instance those 80 in. in diameter weighing some 400,000 lb. and possibly 30 ft. high, have the lower half or one-third bottom poured and the upper part top poured. The bottom pouring forms a pool which completely obviates the splash when top pouring is commenced and continued throughout the ingot to its completion. In the pouring of such large ingots, more than one ladle is necessary. This combined bottom and top pouring method is easy of accomplishment and the results are eminently satisfactory.

Small ingots are top poured, first, because with them the proportion of runner metal which would have to be scrapped were they bottom poured would be greater than with large ingots. It would indeed be prohibitory in the case of very small ingots. Second, because with them the piping tendency is greater, and hence needs to be counteracted by adding the last of the hot metal at the top, as in top pouring; and third, because the cutting of the mold bottom by the falling stream of metal is less than with large or at least high ingots.

It is in harmony with the second of these three reasons that relatively small ingots of boiler-plate steel are top poured. These are freed from piping by refining the steel only imperfectly, so that it gives off enough gas in solidifying, and thus puffs out the progressively thickening walls of the ingot enough, to make up for and efface the pipe-forming tendency. Hence they are not in need of the pipe-closing effect of adding the last of the hot metal at the top as in top pouring. These blowholes are tolerated in this specific case, because the steel is of such low carbon content that they weld readily,[8] and because even if unwelded they would be relatively harmless in view of the direction of the chief stresses in the boiler plate in service.

The pouring of large ingots, on the other hand, is from the bottom, because the three reasons just given for the top pouring of small ingots apply to them with much less force, enabling us to get the great advantages of bottom pouring.

Finally, the pouring of very high ingots begins at the bottom, because the impact of the falling stream on the bottom of the mold in top pouring would be extremely severe; but their upper part is top poured, because the hydrostatic pressure on the joints at the mold bottom and in the runner bricks would be excessive, leading to great danger of "run-outs" from the breaking through of the molten metal. When we cease pouring from the bottom and begin pouring from the top, the metal in the runners and

[8] H. M. Howe: *Proc.*, Amer. Soc. Test. Mat. (1910) **10**, 169.

along the joints at the bottom of the mold freezes, and seals in the molten metal.

In the case of all ingots having brick-lined sink heads, only the body of the ingot is poured from the bottom, and the sink head is poured from the top. This applies more particularly to ingots of 26 in. diameter and upward. Below this point, the sink head is also usually poured from the bottom, because the molds are poured in groups.

56. *Ratio of Thickness of Ingot to Length.*—(*a*) This is given approximately by the following table:

4 in. ingots: length may be as much as 9 times the thickness.
18 in. ingots: length may be 3½ to 5 times the thickness.
40 in. ingots: length must not be more than 2½ times the thickness.
60 in. ingots: length should not be more than 1¾ times the thickness.

If the 40 and 60-in. ingots are intended for shafts, the length may be increased somewhat beyond these ratios, because inclusions are not so harmful in shafting as in guns.

(*b*) These ratios apply primarily to tender steels, for instance alloy steels and others of high carbon content. A greater ratio of length to diameter is often used with advantage for soft steels, especially for those not subject to marked segregation, and in cases in which a long ingot is worked more advantageously than a short one to the size and shape of the objects for which it is intended.

57. *Stripping and Cooling the Ingots.*—Because the tendency to form both pipes and internal and external cracks is due to the faster cooling of the outer than of the inner parts of the ingot, and because this tendency increases with the rate at which the whole is cooled, it should be lessened by retarding the cooling. The first step in this direction is to strip the ingot as soon as its solid walls have grown so thick that they can be trusted not to crack under the hydrostatic pressure of the molten steel.

The cooling may now be further retarded by burying the ingot in ashes, though bituminous coal has been successfully used for this purpose. This intermediate rate of cooling is much better than the still slower cooling in soaking pits, which increases needlessly the coarseness of the dendritic structure, and the degree of interdendritic segregation, and hence of banding, and perhaps also of axial segregation.

Top-poured ingots may often be allowed with advantage to cool in the air between the time of stripping and that of burying in ashes. In order to understand this, let us recall the three successive stages in solidifying:

A. When the solid crust is only a thin skin;

B. When this crust has become strong enough to be left unsupported by the mold;

C. When the solid walls themselves have become so thick that the resistance which their deeper seated, and hence more slowly contracting, parts offer to the faster cooling of their own crust threatens to stretch it too far and thus crack it, unless by retarding the cooling in general we reduce within harmless limits the difference between these parts in their rate of cooling.

Clearly it is not till period *C* that the cooling needs to be retarded artificially. When the ingots are top poured, it may be a convenience to strip them at a relatively early stage of period *B*. During the rest of this period they may be allowed to cool in the air without harm, and thus it comes about that the cooling may consist of three distinct stages:

1. In the mold, while the crust is too thin to be left unsupported;
2. In the air, till the resistance of the deeper seated layers threaten to crack the outer layers; and,
3. In ashes or their equivalent from this time on, till the ingot has cooled so far that the difference in the rate of contraction even in air cooling, between the outer and the inner parts, is too slight to cause danger of cracking the outer crust.

The relatively rapid air cooling stage 2, may save much time.

58. *Heating Ingots.*—Very great care should be taken to raise the temperature of ingots extremely slowly, lest the heating and expansion of the crust outrun that of the deeper seated parts so much as to stretch them beyond their powers of endurance, and thus to cause internal cracks. Even blooms of the tender steel used for cannons should be heated very slowly for the same reason. Their corners should be rounded lest they become burnt in heating.

Very much more detail then is here set forth is involved in the many items of actual practice found necessary to secure satisfactory results in the making and handling of so-called "fine steels," especially when the larger masses are considered, and these for very special uses.

DISCUSSION

W. J. Priestley,* South Charleston, W. Va.—What is the maximum reduction for a gun forging from the ingot to the finished forging?

W. P. Barba.—The specifications for gun forgings were drawn up about 30 years ago for the old-fashioned hammer, where the size of the hammer and the weight of its blow delivered to the piece was an important function in the successful production of the article. Today, with a press, the specifications for reduction of area during forging do not have the same value and I would not hesitate to make a 6-in. diameter forging from an ingot which would give only a 1¾ : 1 ratio of reduction during forging, provided I have good, sound, well-melted steel and must make no discounts whatever on the steel. In the case of the larger forgings,

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the penetrative power of the forging tool is an unknown factor, so it would be proper to insure a little different ratio of reduction of area during forging.

HAAKON STYRI,* Philadelphia, Pa.—It is quite evident that the elimination or burning out of the carbon will depend on the concentration of carbon in the steel, as well as on the concentration of iron oxide in steel, or iron oxide in the slag which will be in certain proportions to one another. The amount of iron oxide in the slag will depend (besides what is mentioned in the paper) on the temperature and the rapidity with which the steel has been melted.

Some years ago in Pittsburgh, with the same furnace and exactly the same practice, on a humid rather warm day, it took a long time to get the steel melted. The iron-oxide content of the slag, when the bath was melted, was about 28 per cent. A few days later, on a cold crisp day, the temperature got high quickly, but the slag melted down to about 42 per cent. iron oxide. This latter burned out the carbon much more quickly than the first, and showed a rapid drop of carbon in the steel. I refer to this because the paper mentions the necessity or the desirability of oring. If a slag that melts down to 40 per cent. oxide is ored, the iron-oxide content will be so high that the drop in carbon cannot be stopped in time to get the carbon content desired with an otherwise finished bath.

If there is a certain amount of oxygen in the steel bath, that oxygen will have a certain dissociation pressure, which will increase with the oxygen content. If any other metal is present in the steel and can react with the oxygen, as for instance manganese, the amount of oxygen that can be in equilibrium with a certain amount of manganese will depend on the manganese content of the steel. I refer to manganese because the authors say that manganese is a stronger deoxidizer than silicon. I would like to ask on what proofs that statement is based. The similar dissociation pressure for oxygen in the presence of silicon in the bath would show an equilibrium curve far below the curve for the manganese. The carbon curve is a little higher than silicon for small concentrations, but lower for high concentrations, which readily explains why, at a certain carbon content, carbon will reduce silicon back in the bath.[9]

The paper also states that the deoxidation should be done with carbon. I agree with this, also with the emphasis laid on the necessity of boiling, because that is the best reaction for removing the non-metallic impurities from the bath. Just as dust particles in the atmosphere are carried downwards by the rain, so are slag inclusions carried upwards by the gas bubbles. For that reason, boiling is always advisable, especially for

* Chief of S. K. F. Research Laboratory.

[9] *Chem. & Met. Eng.* (May 1, 1919) **20**, 482.

nickel steels. I believe that the high viscosity of the nickel steels is, to a certain extent, responsible for the difficulty of refining.

The first gun steel made in this country during the war passed inspection, but at practically the same time numerous plants got rejected material. Possibly this was because nickel scrap was remelted, so that there was a high nickel content from the beginning, which gave a more viscous bath, with the temperatures then used for refining. The plants learned later the necessity of increasing the temperature.

The authors mention the desirability of deoxidizing the foreign oxygen with the silicon, after the carbon has done its duty. They state that silicates are formed when manganese is added before silicon, and apparently mean that if silicon is added first, silica and not silicate will be formed. I consider this impossible, referring to the laws of mass action. I believe that when silicon is added to a bath containing oxygen, silicate is formed. If no manganese is present, iron silicate will be obtained; if manganese is present a combination of iron and manganese silicate will be formed but this will not go to the bottom of the hearth. It will be of great interest to know the author's method of proving the presence of metallic silicon beside silica or silicates.

It is a question whether silicon or manganese should be added first as a final deoxidizer. It is probably best to add silicon, because it is more important to keep the correct amount of manganese in the bath than it is to keep the correct amount of silicon. Any silicon added beyond the point of equilibrium with oxygen will combine with oxygen and be especially effective if there is some manganese in the bath.

I call attention to the importance of watching the dampers and valves for air and gas supply, because the furnace atmosphere has a great influence on the slag condition. If it is strongly oxidizing, the slag will take up much oxygen and throw the reaction in the bath off balance so that it may be impossible to finish the steel properly.

C. T. PATTERSON,* Syracuse, N. Y.—The heat of formation of SiO_2 is considerably greater than that of 2MnO, therefore in the basic furnace silicon will reduce manganese in the slag and silicon dioxide will be formed, but in an acid furnace for automobile castings, the reaction was found to go the other way. Silicon dioxide in the slag oxidized the manganese in the metal, thereby increasing the silicon in the metal while the manganese in the metal decreased and MnO in the slag increased, all at the same time with a reducing atmosphere in the furnace. This effect was very pronounced in the second ladlefull, which was always held 20 to 30 min. in the furnace while the first ladlefull was cast. In searching for an explanation, it was found that the heat of formation of manganese silicate was much greater than that of silicon dioxide.

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* The Solvay Process Co.

HARRY BREARLEY, Sheffield, Eng.—The casting temperature of steel is not the temperature of the steel in the ladle. It is possible, by casting a very hot heat of steel slowly, to produce the same result in the final ingot as would be obtained by casting a comparatively cold heat of steel quickly. From a practical point of view, it is well that this is so, because when a steel maker gets, into the ladle, steel that he feels is too hot, he should have some way of pouring this material so as to produce a satisfactory ingot.

The real casting temperature, that is that temperature which determines the type of crystal growth and the mechanical strength of the ingot, is the temperature of the material as it lies quiescent in the ingot mold. Perfectly satisfactory ingots can be produced from very hot material (for example, very hot bessemer blows), if the speed of casting is such that when the mold is full, the temperature of the steel in the mold is not above a reasonable casting temperature.

Another consideration is the control of the casting temperature by observation of the metal in the mold. To produce mechanically strong ingots, steel should be poured into the mold at such a rate that it is freezing over on the upper layer, which condition is most easily observed and controlled when ingots are bottom cast. The great disadvantage of bottom castings is that the steel is more likely to contain dirt. At the plant with which I am associated all the molds are cleaned with a vacuum cleaner immediately before the ingots are cast. A notable advantage of bottom casting is that the ingot is really cast in the mold; that is, the interior of the mold shapes the ingot. In top casting, particularly from heavy charges out of large ladles, the ingot is not shaped by the interior of the mold.

In the case of an ingot top-cast from a ladle containing a great weight of material, the impact of the fluid stream on the surface produces considerable motion, so if the casting were stopped at any particular moment, there would be a sort of fringe above the normal level of the ingot. That particular fringe, which I have called the "swirl envelope," is formed from almost the bottom to very near the top of the ingot and is the fluid metal that swirls up the side of the ingot mold and solidifies. Solidified steel, when hot, readily oxidizes; consequently the surface of that swirl envelope above the normal level of the fluid steel is oxidized. We know also that when fluid carbon steel comes into contact with oxide of iron, gases are formed; consequently when the fluid steel rises over the swirl envelope small quantities of gas may be liberated at the side. The ingot is not shaped by the side of the ingot mold, but by the swirl envelope that immediately precedes it.

Any small blowhole forming on the interior surface of the swirl envelope may make its way toward the center of the ingot and escape; and it may not. If the steel has been cast reasonably hot, you get first a

mass of very small crystals that have frozen very quickly, representing the swirl envelope; then you get a number of chill-crystal dendrites, then in the interior of the ingot a number of equiaxed crystals, or what are called free crystals. As the ingot is being poured, the chill crystals that have already formed are beginning to cool and contract. As the original chill crystals were much purer than the mother liquor from which they were formed, each is surrounded by an envelope of impure material; so when they squeeze together, the enveloping material is pushed in the direction in which it can travel most easily, which generally is into the interior of the ingot. But if there are small holes behind the chill crystals, there is no reason why that impure mother liquor should not be forced back into those small holes. Therefore, while in cutting up an ingot one does not find as large a number of small holes adherent to the swirl envelope as might be expected, almost invariably in the top-cast ingot around the inner edge of the swirl envelope there will be a number of small segregates, indicating impurities squeezed into the holes from between the chill crystals.

I agree with the statement that as good steel can be made in America as anywhere; but it will be necessary to take the precautions that people take elsewhere. Good steel making is not always consistent with very high tonnage.

A good deal has been said about clean steel. One of the difficulties, in talking about clean steel, is that our laboratories cannot express the degree of cleanness in concrete figures. If they could, we would know much better what we were talking about, because whether unclean steel is a disadvantage or not depends largely on the purpose for which that steel is to be used. However, it is possible, by mechanical methods, to express the relative freedom of steel from non-metallic impurities, in concrete figures. The relation between the figure obtained on the longitudinal impact piece and the figure obtained on the transverse impact piece is, roughly, a measure of the cleanness of the steel; the transverse figure is never as high as the longitudinal figure, sometimes it is ten times less. If the steel is for high-class purposes, such as ball races, where the transverse strength of the material is very important, the transverse impact figures should not be less than one-half the longitudinal.

Almost all over the world people have been led to the conclusion that nickel steels are particularly apt to contain slag inclusions; this is untrue. Nickel steels do not contain more slag inclusions than ordinary steel, if they are made in an equally good way. The reason that they appear to contain more slag inclusions is this: A slag inclusion is a discontinuity in the rolled bar in which it exists; a seam also is a discontinuity. That discontinuity is not evident until the bar is distorted. These small discontinuities in material due to the slag streak are more apparent in nickel steel than in ordinary steel because nickel steel distorts more before treating.

W. P. BARBA.—As was just said, nickel steel is exactly like carbon steel when it is in the furnace. It is possible to make just the same mistakes on carbon steel as are made on nickel steel. The question of difference of viscosity during melting of nickel steel is not worth mentioning in a furnace powerful enough to do the work. In the case of mixtures of more easily oxidizable materials, such as chromium and its near relations, there is an entirely different condition during melting, but that condition is easily transmitted almost immediately into the slag and has nothing to do with the fluid metal below.

In splitting ingots varying in size from 2-in. cubes up to 150,000 lb. and more, I have found the conditions stated by Mr. Brearley, except the squeezing of the rich mother liquor back into a cavity formed by an accidental ebullition of gas. The thing that he described, of course occurs. We have all seen what Doctor Howe has called, "interdendritic segregation," even to a point where an analysis, carefully sampled of course, will show 0.04 per cent. phosphorus, with its attendant sulfur and carbon in one spot, and 2 in. away I have seen 0.120 per cent. phosphorus with its attendants. No doubt, the 0.120 per cent. was one of these blowholes that was filled by being squeezed full of rich mother liquor. That mother liquor also can be trapped by the enormous plates of crystals that form in a hot-poured ingot. The result is a streaky forging.

The temperature of pouring is unquestionably indicated in this paper as the temperature of the metal in the mold. It states that when pouring the carefully melted steel into the carefully prepared mold, the man best equipped by judgment and experience should determine the rate of pouring of the metal into the mold, according to the appearance of the metal as it rises. Medium-weight ingots, say 100,000 lb., should be bottom-poured so that this can be done.

The paper gives suggested weights of ingots that can be most economically, for most purposes, poured from the bottom, from the top, or from a combination of both. But observation, experience, and accurate records of every ingot as it is charged, melted, refined, and poured are necessary to pour large ingots successfully. There are two kinds of dirt, mechanical and chemical. It is easy to determine the presence of chemical dirt with a low-power microscope because such dirt is widely and uniformly distributed. Mechanical dirt is largely accidental; the difference between the two is easily distinguished by those who have made many observations.

In regard to Doctor Styri's statement, the paper is incomplete in that we did not say that silicon would be reduced from the "hearth and slag or any other contributing cause." The hearth means everything surrounding the metal. Ferrosilicon or ferromanganese, when added to a molten bath, do not go to the bottom; they float of course. Equally is it true that we would rather refine by the use of manganese on an

acid bottom than by the use of silicon, because we can get a further reduction of oxygen, but it promotes the formation of manganese silicate in large volume and weight. The paper recommends the use of silicon solely to avoid the encouragement of the formation of manganese silicate, which would be found as spots in the finished product and would be a compromise between chemical dirt and mechanical dirt for it arises from both in that it clears from the molten metal with difficulty.

Doctor Styri called attention to extreme conditions within a few days in the same furnace, when one heat was a long time melting, and slag contained 28 per cent. oxide of iron. I would not try to make fine steel out of such a heat; I would get rid of it. It is possible to add something to such a heat to get it back into something like condition; the most practical thing is to pour a ladle of melted cast iron into the furnace and raise carbon, silicon, and temperature. Melted cast iron is the surest cure for the condition described, but even then I would not put this metal into fine steels but would shunt it into ingots for less important purposes.

When making nickel steel, in the early days of the E. F. Wood patents, we melted our pig and scrap, and as soon as the heat was melted put in, with the charging machine, barrels of nickel oxide. Metallic nickel was difficult to get; but nickel oxide was plentiful. It was not much later that the Bethlehem Steel Co. suggested adding the nickel to a percentage below that needed in the final product, and after an analysis in the laboratory, preliminary to tapping, correcting up to the minimum nickel that is allowed by the specifications. With the improvements in method of reducing oxide to pig nickel, all that became easy. There is no difference whatever, except economy and ease, whether the nickel is added during the operation or at the beginning.

This paper mentions, but does not discuss, the fact that 11 per cent. ordinary ferrosilicon can be added in large quantity in basic furnaces for these same final carburizing reasons; I do not think that we should take the time to discuss whether manganese in a basic furnace is an acid or a base. Sometimes I am convinced it is either or both in turn. But as we are discussing a paper on acid practice, I want to affirm once more that silicon is not the thing we would like to use for deoxidizing purposes, but it is the thing that we should use, rather then manganese, for the sole purpose of avoiding the formation in large quantity of manganese silicate where the conditions will promote that formation.

The paper requires that ore should be added for a specific purpose, also that standardized conditions be maintained for the production of steel of fine quality uses and purposes. In a heat, when melted of good material, in good standard time and standard condition, I strongly urge the use of a little ore to promote ebullition to get the lagging oxide materials up to the slag, and then through the slag.

W. J. PRIESTLEY.—All of the steel that we have made within the last year has been top poured. We tried bottom pouring and had inclusions; we got poor test bars and flake. We thought that the flake was probably due to hot steel, but to bottom pour without freeze ups, it was necessary to pour hot. We tried top pouring slowly at the rate of a ton a minute, through a 1-in. nozzle. In our efforts to reduce the temperature, we had to increase the size of the nozzle; we tried to pour at not over 2800° F. A record is made of the reading of the optical pyrometer of every heat taken out of the electric furnace. When the steel is teemed into the mold, the temperature is again taken and recorded. In addition, a detailed melt log is made of every step, from the charging of the ingredients into the open-hearth furnace through the electric; so that if there is trouble in the heat treatment, we can frequently lay our finger on the trouble and its source.

It was doubtful whether we would be able to top pour a 100-ton heat for 68-in. ingots and 100-ton ingots for armor plate. Some of the armor-plate ingots cast in iron molds had a depth of 20 ft. The ingots were 43 in. thick and 110 in. wide and could not be poured successfully with a 1½-in. nozzle. Pouring so cold caused a crust to form on the top of the metal in the mold; so we had to use a 2-in. nozzle, and then it was necessary to break the crust as the steel rose in the mold. The first two ingots cast tore in the corner, but there were no surface tears. By breaking up this crust and bringing up the oxides of iron that probably formed there we were able to forge the ingots completely without any tearing.

We thought, at one time, that flake in electric steel was due to the sudden cooling of the ingot or to the fact that it was allowed to cool down entirely after casting. Our present practice is to get it out of the mold as quickly as possible, heat it for forging, and after forging put it into the annealing furnace before it gets much below its critical point.

It has been our experience that carbon steel, manufactured in exactly the same way, melted, poured, etc., in the same way as nickel steel, will stand a whole lot more rough usage than nickel steel; this is particularly true of the electric steel.

We have used in our open-hearth furnaces pig iron and 60 per cent. of nickel scrap; we have used various amounts of carbon scrap and nickel-chrome scrap, but except for the condition in the slag in the nickel-chrome heats, we have never noticed any difference in the final working of the steel.

Reference has been made to the value of the impact shock, and breaking tests. We planned to develop these tests in Charleston, but were unable to carry out our plans. We made many cold-bend tests together with tensile tests and found that tensile bars showing 45 to 50 per cent. reduction of area would rarely, if ever, break in a cold bend. They could be bent double on themselves without any trouble.

Reference has been made to the form of the corrugations on ingots. We first used sharp corrugations but occasionally got corner cracks or cracks in the corrugations. At one time, the sharp corrugations on the ingots were very deep seated; in some cases they were 2 in. below the surface of the ingot. Forgings made from them on 40-in. ingots frequently would show no signs of the cracks until the piece was being machined and ready for heat treatment, when sharply defined cracks appeared exactly where the corrugations were. We found that by increasing the radius of the corrugations, the ingots were not as tender nor as susceptible to cracking or segregation.

We lay great stress on the temperature control of our steel, both in the refining and in the teeming.

GEORGE F. COMSTOCK,* Niagara Falls, N. Y. (written discussion).—In paragraph 31 aluminum and titanium are classified together, with other metals, as deoxidizers that are also of use as alloying elements in steel, and the products of the oxidation of which tend to form inclusions in the steel. It is true that both aluminum and titanium are deoxidizers, but it is surely an exaggeration to state that they have a growing use as alloying elements in steel. The similarity between these two metals, in connection with steel making, ceases abruptly at this point. It is well known that aluminum has such a marked tendency to leave alumina inclusions in steel that its previous use can nearly always be discovered by a microscopic search for such inclusions in a polished section of the steel. It is equally true that titanium does not contaminate with its oxide the steel in which it is used. In this respect it differs markedly from silicon as well as aluminum, and I protest against these elements being grouped together in this respect.

The authors' denunciation of the use of titanium and other deoxidizers beside silicon and manganese should be definitely understood as applying, according to the authors' statements, to only the special steels for ordnance purposes where time and expense of production are not taken into consideration. It may be admitted that under such conditions the use of titanium might be superfluous. But this should not be taken to imply a similar condemnation of its use as an aid to quality under ordinary practical steel-plant conditions, where speed and cost of production are vital factors. Under such conditions the experience of numerous steel makers has shown that titanium may be an almost indispensable addition to finish the steel properly, and that its use does not involve contamination of the metal in any way.

ALEXANDER L. FEILD,† New York, N. Y. (written discussion).—

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In paragraph 30 (*i*), the authors state that manganese is a stronger addition than silicon, or words to that effect. Reading into this statement the meaning that the context would appear to give it, one might be led to conclude that manganese exhibits a greater affinity for oxygen than does silicon, in the conditions prevailing in Period V. As silicon is known to reduce the oxides of manganese at high temperatures and as this reaction can be made to go to practical completion, it is doubtless true that the authors do not refer to the relative affinities of manganese and silicon for oxygen. However, the general term of deoxidation has come to include not only reactions between the addition agent and metallic oxides but between the addition agent and the various gases dissolved in steel. Even if the authors' statement is taken to include the degasification of steel, there is abundant proof that silicon is a more powerful agent than manganese. Brinell, in his work on the influence of chemical composition on the soundness of steel ingots, came to the conclusion, based on long and practical experience and on exhaustive research, that silicon has 5.2 times the solidifying power of manganese. The writer has had occasion recently to check up this conclusion of Brinell and is able to report that it fitted the observed facts with a relatively high degree of accuracy.

Is it not true that the authors, in stating that manganese is a stronger addition than silicon, refer to the fact that a manganese addition, made after the silicon addition and not long prior to tapping, promotes the formation of a fusible, fluid manganese-silicate slag? This fusible slag, due to its low viscosity, readily agglomerates into relatively large globules which rise to the top of the bath and enter the slag layer. Such has heretofore been the current explanation of this cleansing action of manganese upon a steel deoxidized first with silicon and of silicon upon a steel deoxidized first with manganese. The fact that there is a loss of manganese is no proof that manganese has performed an additional work of deoxidation upon the metal bath. Such a loss is properly attributable to oxidation of manganese by the slag and to mechanical losses.

Application in Rolling of Effects of Carbon, Phosphorus, and Manganese on Mechanical Properties of Steel

By Wm. R. Webster, Philadelphia, Pa.

(New York Meeting, February, 1922)

This is a contribution for the proposed new discussion on the physics of steel. The former discussion on the subject started with the consideration of five papers presented at the Chicago meeting in 1893, and continued for several years. The Suggested Lines of Discussion, prepared by Doctor Howe, covered a wide field and added greatly to the success of the work. Naturally, the first step in a new discussion will be to remodel and bring up to date the old Suggested Lines of Discussion so as to embody all the important advances in the metallurgy of steel that have a bearing on the physics of steel and keep the papers and discussions within the field of work undertaken. This paper will be devoted to the practical application, in rolling steel, of the effects of carbon, phosphorus, and manganese on its tensile strength, with some suggestions on further research work.

Dr. J. E. Stead, in his paper Influence of Some Elements on the Mechanical Properties of Steel,[1] gave a complete review of all that had been done during the past thirty years. He gave full credit to all investigators who worked on these lines, also their results, with his views on same, and in many cases his own results. All of this data and much new valuable information were put in convenient shape for reference and study. To do this required a great deal of work, which is fully appreciated by the steel manufacturers and investigators.

The variations in the values given by the different investigators for the increase of the tensile strength of steel for each 0.01 per cent. of carbon, phosphorus, and manganese were largely due to the steels they worked on, the large or small variations in the amount of the elements present, and the omission to take into consideration all the factors, from the blast furnace through to finished rolled material, that affect the character of the steel. For instance, a poorly made dirty steel requires considerably more carbon to give the same ultimate strength than a well-made clean steel with the same phosphorus and manganese content.

[1] *Jnl.* Iron and Steel Inst. (1916) **44**, 5.

None of the values given for each element will apply equally well for all makes of steel or to different works making the same steel, yet each of us has contributed something to the fund of information that has enabled the present practical steel grading methods to be developed. Of course, the development of the quick chemical methods has greatly assisted in this work, especially the quick combustion for carbon determination, which has generally replaced the old color carbons, which at times were more or less guess work. Fortunately, several of our largest steel manufacturers have always relied on the work of different investigators and coöperated with them. These manufacturers deserve credit for this and the practical working tables that have been developed and put into daily use at their works. They can now grade their steel and roll it into the finished product with much greater certainty of its meeting all requirements of the standard specifications than formerly and with much less trouble than when they had to grade the steel from the results of the tension and bending tests of bars rolled from small test ingots from each heat of steel.

Should trouble occur under the present method of working, its cause is more easily located and corrected, as we now appreciate that uniform results can only be obtained by proper heating with proper reductions and medium finishing temperature in rolling. More good steel was formerly spoiled by too heavy reduction and by too high finishing temperatures in rolling than from any other cause.

Base for Structural Steel Calculations

When bessemer steel was in general use for structural purposes, a base of 50,000 lb. per sq. in. (3515.4 kg. per sq. cm.) was taken, to which 1000 lb. (453.6 kg.) was added for each 0.01 per cent. of carbon contained in the steel. This worked fairly well as a guide, the base being high enough to include the effect of the average manganese and phosphorus contained in the steel, but the results of tension tests of bars rolled from small test ingots necessarily were used for grading the steel. When acid open-hearth steel came into use, the base of 50,000 lb. (22,679.6 kg.) was found too high. In 1885, Mr. Salom wrote as follows:

> The influence of carbon on steel is better known than that of any other substance which enters into its composition. No one, however, so far as I am aware, has done anything more than formulate the general law that tensile strength increases with carbon, other things being equal. I have made the interesting observation that this increase is almost exactly 1000 lb. for each 0.01 per cent. of carbon. That is to say, assuming 0.01 per cent. of carbon to be a unit of carbon, if to 45,000 lb. (20,411.7 kg.) (the tensile strength of pure wrought iron) we add as many thousand pounds as there are units of carbon, we shall be able to make a close approximation to the tensile strength. Boiler-plate steel, for example, has about 0.15 per cent. carbon, and 15,000 plus 45,000 equals 60,000 lb. or about the tensile strength of boiler-plate steel, etc.
>
> Of course this law only holds good where other things are equal. An undue amount of one or all of the foreign substances that enter into the composition of steel or unusual physical conditions, would change the results entirely. It may be of value

however, as an indication that, when steel with a known amount of carbon does not possess a certain tensile strength, the other substances entering into its composition are present in undue proportion, or it must have been made under unusual physical conditions.

The above law is not applicable to castings, where the presence of so much silicon affects, in a notable degree, the tensile strength derived from a given amount of carbon, and the physical properties are also affected by the fact that the metal has not been worked.

Mr. Salom did not give any value for the effect of phosphorus or manganese, and the tension tests of bars from small test ingots were used, as before, for grading the steel and applying it on the orders.

The conditions were practically the same in 1892, when the writer began his investigation at the Pottstown Iron Co.'s works, except that the introduction of basic steel, with much lower phosphorus, had shown that the base of 45,000 lb. (20,411.7 kg.) was too high. No additional information on the effect of carbon was available and the information on the effect of manganese and phosphorus was conflicting; the writers generally claimed that there was no relation between the chemical composition and mechanical properties of steel that could be relied on. This added to the interest of the problem undertaken.

Effect of Finishing Temperature and Thickness of Rolled Steel on Tensile Strength

At that time there was no general knowledge of the effect of finishing temperature and of the thickness of rolled steel on its tensile strength; if the steel manufacturers had such information, they kept it to themselves. To determine these questions, to be used as a starting point, a large number of slabs from the same heats of steel were rolled into plates of different thickness; the finishing temperatures of these plates were kept as nearly uniform as possible for each thickness of plates rolled. The tension tests showed that there was a decrease of 1000 lb. per sq. in. for each increase of $\frac{1}{8}$ in. (3.17 mm.) in thickness of plate from $\frac{3}{8}$ in. (9.52 mm.) upward, and an increase of 1000 lb. for each decrease of $\frac{1}{16}$ in. (1.59 mm.) down to $\frac{1}{4}$ in. (6.35 mm.) thickness. This accounted for some 6000 lb. variation in the tensile strength of plates rolled from the same heat of steel, depending merely on the difference of the thickness into which the plates were rolled.

The importance of this is shown when we consider that there is only a range from about 45,000 to 85,000 lb. (3163.9 to 5976.2 kg. per sq. cm.) tensile strength of steel used for structural purposes, and that 15 per cent. of this 40,000 lb. difference is accounted for by the difference in the results from the same heat of steel when part is rolled into thick and part into thin material.

These results formed a good sound basis for all the work that followed and helped materially, as they covered the effects of about six to eight points of carbon. The writer at that time also found that the elongation

and bending properties of rolled steel also depended greatly on the reductions in rolling, section rolled, finishing temperature in rolling, and rate of cooling. These points are well recognized today, and some of the mills take precautions in winter to keep the drafts of cold air from coming in contact with hot steel on their cooling beds; this is more important for the high than for the lower carbon steels.

The values referred to are in general use today with slight modifications to meet the special conditions at the different mills and the classes of material rolled. Some of the mills now follow a more direct method and, from their own records, increase the carbon as the thickness of their material increases on the same general plan as Doctor Stead refers to:

In works where ship and boiler plates are produced, widely varying results are obtained with the same steel if it is rolled into plates of varying thickness, but this is due to mechanical work and variation in finishing temperature. The more work and the lower the finishing temperature, the higher will be the tenacity.

In order to get the same static tests in ship plates of varying thickness, the carbon must be higher in the thicker plates. For instance, to meet Lloyd's specification and tests the relation between carbon and thickness of plate is as follows:

	Per Cent.		Inch
Carbon	0.12 to 0.14	Thickness of plate	3/16 to 5/16
Carbon	0.15 to 0.17	Thickness of plate	3/8 to 1/2
Carbon	0.17 to 0.21	Thickness of plate	1/2 to 1
Carbon	0.21 to 0.24	Thickness of plate	1 to 1 1/2

If all these plates were normalized at 900° C. and cooled at the same rate, the tensile properties would vary proportionally with the carbon.

This table shows that a wide range of carbon limits must be used to keep the ultimate strength of plates from 3/8 to 1½ in. (9.52 to 38.099 mm.) in thickness within the required limits of the specifications. Particular attention is called to this, as some engineers still hold to the old idea, and claim that steel from the same heat should meet all of the requirements of their specifications, irrespective of the difference in thickness of plates or weight of shapes that it may be rolled into.

Webster[2] estimated the ultimate strength for pure iron, if it could be obtained, as 38,000 lb. per sq. in. (2671.7 kg. per sq. cm.) and to this base added the effects of the other elements. This low base for pure iron was confirmed, in 1895, by Campbell,[3] when he used 37,430 lb. for basic steel and 38,600 lb. for acid steel, and more recently by Arnold, Brinell, Stead, and others, which is very gratifying to the writer.

Webster's value of 800 lb. per sq. in. (56.25 kg. per sq. cm.) for each increase of 0.01 per cent. carbon was confirmed by Campbell in his second

[2] *Trans.* (1892) 21, 766. Webster's first paper. The effects of carbon, manganese and phosphorus are taken from same paper, the effect of sulfur not being considered, as most of the more recent investigations by others have shown that the effects of the ordinary content of sulfur are negligible.

[3] H. H. Campbell: "Manufacture and Properties of Iron and Steel." New York, 1904. Eng. & Min. Jnl. Co.

investigation, in 1904, when he used 770 lb. for carbon by combustion and 820 lb. for carbon by color for basic open-hearth steel. Doctor Stead gives carbon an effect of 870 lb. per unit of 0.01 per cent. All of these values are considerably lower than the old value of 1000 lb. per unit for all makes of steel.

Webster's values for the effect of 0.01 per cent. phosphorus starts with 800 lb. per sq. in. in the presence of 0.08 per cent. carbon and increases to 1500 lb. (105.5 kg. per sq. cm.) in the presence of 0.15 per cent. carbon or over, that is, from the same effect as carbon to 1⅞ times the effect of carbon.

Campbell, in his first investigation, gave 950 lb. as the effect of 0.01 per cent. phosphorus for basic steel and for acid steel 1050 lb. In his second investigation,[4] he gave 1000 lb. for each 0.01 per cent. phosphorus for both acid and basic steels.

Doctor Stead states: "In reviewing the work of Stead and d'Amico, that the effect of 0.10 per cent. phosphorus is comparable within certain limits with that of carbon."

In mill work, when grading good basic open-hearth steel, there is little need of considering the differences in the effects assigned to the unit of phosphorus, as the phosphorus in this steel does not generally vary more than four points, while the additions to the tensile strength, when estimated by the different methods referred to, varies from about 1500 to 3000 lb. per sq. in. Most of this is generally covered by the differences in the values given to the effects of manganese and carbon. Satisfactory results are obtained in rolling steel under all of these varying methods.

There has always been a great difference in the opinions of investigators and manufacturers of steel regarding the effect of manganese on its tensile strength. Some claim that the effect was slight, others that there was no effect on basic open-hearth steel until the manganese was above 0.40 or 0.60 per cent. but most of them admit its effect on acid open-hearth steel. Webster's values for manganese varied, decreasing per unit as its content increased. He found the effect on basic open-hearth steel was less than on basic bessemer steel. In part they were as follows:

	Lb. per Sq. In.
Basic open-hearth steel with 0.35 manganese, 0.01 per cent.....	163
Basic open-hearth steel with 0.55 manganese, 0.01 per cent.....	151
Basic bessemer steel with 0.35 manganese, 0.01 per cent.....	223
Basic bessemer steel with 0.55 manganese, 0.01 per cent.....	189

Vosmaer in 1891, in Mechanical and Other Properties of Iron and Steel, gives the effect of:

0.01 per cent. of carbon as 853 lb. per sq. in.

0.01 per cent. of phosphorus, one-fourth the effect of carbon, as 213 lb. per sq. in.

0.01 per cent. of manganese, one-fifth the effect of carbon, as 170 lb. per sq. in.

[4] *Trans.* (1905) **35**, 772.

Campbell in his first investigation gave, in basic open-hearth steel, 0.01 per cent. manganese a value of 85 lb. He gives in his second investigation[5] complete tables for the effect of manganese in both basic and acid open-hearth steel, showing that its effect per unit increases with the increase of the carbon in the steel.

Cunningham's rule,[6] "To find the approximate tensile strength of structural steel to a base of 40,000 lb. add 1000 lb. for every 0.01 per cent. carbon, and 1000 lb. for every 0.01 per cent. phosphorus, neglecting all other elements in normal steels. Radical variations between calculated and actual strength indicate mixed steels, segregation, incorrect analyses, or unusual treatment in manufacture" was a good guide for basic open-hearth steel, as the base of 40,000 lb. (2812.3 kg. per sq. cm.) was high enough to include the effect of the average amount of manganese in structural steel.

Grading of Steel

During the last seven or eight years, some steel works, from their own data and tension tests of rolled material of different weights and thickness on former orders, have made their own tables for rolling similar materials on new orders. The results are most satisfactory, as the makers have at once the data required to grade and roll heats of steel best suited to comply with the requirements of each order. These tables cover not only the thickness of the steel but all other rolling conditions at the particular mill for which the table is designed. Formerly, it would have been almost impossible to collect such data, owing to the large number of specifications in general use. They were good, bad, and indifferent and covered all sorts of divisions of the steel. Through the work of the Steel Committee of the American Society for Testing Materials steel specifications were standardized and many of the old specifications scrapped. The other engineering societies coöperated in this work, and the whole range of structural steel is now covered by about six subdivisions, the limits of each covering a range of about 10,000 lb. (703.1 kg. per sq. cm.) in tensile strength. Some of these overlap, as for instance, 55,000 to 65,000 lb. per sq. in. overlaps the 50,000 to 60,000 lb. and 60,000 to 70,000 lb. These standard specifications simplified matters very much in every way. The manufacturers have a larger tonnage to make on a given grade of steel than before, and it became easy for them to collect their records of tension tests and compile good reliable working tables. This enabled them to make better and more uniform steel. These tables are generally based on the results of tests made on steel containing not over 0.02 per cent. phosphorus; for higher

[5] *Trans.* (1905) **35**, 772.

[6] *Trans.* Amer. Soc. Civil Engrs. (1897) **38**, 78.

phosphorus, they add 1000 lb. (453.6 kg.) for each increase of 0.01 per cent. of phosphorus.

Steel works *X* uses practically the same form of table, based on records of rolling steel of not over 0.04 per cent. phosphorus, but in applying heats with higher phosphorus it deducts 0.02 per cent. carbon for each increase of 0.01 per cent. phosphorus; that is, it is now using practically the values given by the writer in 1892, when he gave phosphorus 1⅞ times the effect of carbon when it occurred in steels of 0.15 per cent. carbon and over. The grading of steel by these tables has for years given satisfactory results and confirms the work done at Pottstown.

About 1913, steel works *A* took several thousand tests of its ¾-in. round bars rolled from small test ingots of basic open-hearth steel, and grouped the results under each 0.01 per cent. carbon, from 0.10 to 0.75 per cent. inclusive, with the manganese from 0.34 to 0.96 per cent. inclusive, advancing by 0.02 per cent. Mn. The following note is taken from this table: "When phosphorus is greater than 0.02 per cent. the figures should be increased at the rate of 1000 lb. for each 0.01 per cent. that the phosphorus exceeds 0.02 per cent."

The same course was followed with the ¾-in. round tests from its bessemer steel, the carbon limits are the same, but the manganese limits run from 0.34 to 1.16 per cent. As these tables are too large to embody here, the parts covering carbons 0.10 to 0.40 per cent. and manganese 0.34 to 0.60 per cent. are given. The increase in the tensile strength for the 30 points of carbon and 26 points of manganese is 31,455 lb. for basic open-hearth steel and 30,860 lb. for acid bessemer steel.

After several attempts to get a workable table of estimated tensile strengths that would agree with the averages of the actual tests of the basic open-hearth steel given in Table 1, the writer found that by starting with the base given in that table for 0.10 per cent. carbon and 0.34 per cent. manganese, 50,145 lb. per sq. in. (3525.2 kg. per sq. cm.) and giving an increase of 830 lb. (58.36 kg.) for each 0.01 per cent. of carbon and 170 lb. for each 0.01 per cent. manganese, that satisfactory results were obtained.

These estimated tensile strengths are given in Table 3 for each increase of 5 points carbon from 0.10 to 0.40 per cent. inclusive, and for each increase of 4 points manganese from 0.34 to 0.58 per cent. manganese inclusive. For convenience of comparison, the results of the tension tests from Table 1 for the same subdivisions of 5 points of carbon and manganese are given in Table 3, also the differences between the tension tests and estimated tensile strength. The results agree much better than one would expect, and indicate that manganese has a much greater effect than is usually assigned to it.

TABLE 1.—*Steel Works A, Basic Open-hearth Steel*

Phosphorus under 0.031 *per cent.; manganese* 0.34 *to* 0.60 *per cent. varying by* 0.02 *per cent.; carbon* 0.10 *to* 0.40 *per cent. varying by* 0.1 *per cent. Average of actual tensile strength of* ¾*-in. round test bars rolled from test ingots.*

When phosphorus is greater than 0.02 *per cent. the figures should be increased at the rate of* 1000 *lb. for each* 0.01 *per cent. that the phosphorus exceeds* 0.02 *per cent.*

Per Cent., Carbon	Per Cent., Manganese													
	0.34	0.36	0.38	0.40	0.42	0.44	0.46	0.48	0.50	0.52	0.54	0.56	0.58	0.60
	Tensile Strength, Pounds per Square Inch													
0.10	50,145	50,595	50,950	51,300	51,700	52,100	52,440	52,720	53,000	53,400	53,800	54,200	54,600	55,000
0.11	51,410	51,790	52,090	52,390	52,720	53,050	53,340	53,595	53,850	54,245	54,640	55,025	55,390	55,760
0.12	52,675	52,980	53,235	53,480	53,740	54,000	54,245	54,470	54,700	55,090	55,485	55,850	56,185	56,520
0.13	53,945	54,175	54,375	54,570	54,760	54,950	55,145	55,350	55,550	55,940	56,325	56,670	56,975	57,280
0.14	55,210	55,370	55,520	55,660	55,780	55,900	56,050	56,225	56,400	56,785	57,170	57,495	57,770	58,040
0.15	56,475	56,565	56,660	56,750	56,800	56,850	56,950	57,100	57,250	57,630	58,010	58,320	58,560	58,800
0.16	57,040	57,140	57,240	57,340	57,435	57,530	57,675	57,860	58,050	58,445	58,840	59,180	59,455	59,730
0.17	57,605	57,710	57,820	57,930	58,070	58,215	58,400	58,625	58,850	59,260	59,675	60,035	60,350	60,660
0.18	58,170	58,285	58,405	58,520	58,710	58,895	59,120	59,385	59,650	60,080	60,505	60,895	61,240	61,590
0.19	58,735	58,885	58,985	59,110	59,345	59,580	59,845	60,150	60,450	60,895	61,340	61,750	62,135	62,520
0.20	59,300	59,430	59,565	59,700	59,980	60,260	60,570	60,910	61,250	61,710	62,170	62,610	63,030	63,450
0.21	59,775	60,025	60,275	60,510	60,785	61,055	61,365	61,700	62,040	62,470	62,905	63,320	63,720	64,120
0.22	60,245	60,615	60,985	61,320	61,590	61,855	62,155	62,495	62,830	63,235	63,640	64,030	64,410	64,790
0.23	60,720	61,210	61,700	62,130	62,390	62,650	62,950	63,285	63,620	63,995	64,370	64,740	65,100	65,460
0.24	61,190	61,800	62,410	62,940	63,195	63,450	63,740	64,080	64,410	64,760	65,105	65,450	65,790	66,130
0.25	61,665	62,395	63,120	63,750	64,000	64,245	64,535	64,870	65,200	65,520	65,840	66,160	66,480	66,800
0.26	62,285	63,020	63,755	64,410	64,700	64,990	65,310	65,660	66,010	66,335	66,660	66,990	67,325	67,660
0.27	62,905	63,650	64,390	65,070	65,405	65,735	66,085	66,455	66,820	67,150	67,480	67,820	68,170	68,520
0.28	63,530	64,275	65,020	65,730	66,105	66,480	66,860	67,245	67,630	67,970	68,305	68,655	69,020	69,380
0.29	64,150	64,905	65,655	66,390	66,810	67,225	67,635	68,040	68,440	68,785	69,125	69,485	69,865	70,240
0.30	64,770	65,530	66,290	67,050	67,510	67,970	68,410	68,830	69,250	69,600	69,945	70,315	70,710	71,100
0.31	65,800	66,585	67,370	68,155	68,560	68,960	69,370	69,785	70,200	70,570	70,940	71,305	71,670	72,030
0.32	66,835	67,645	68,455	69,260	69,610	69,955	70,330	70,740	71,150	71,545	71,935	72,295	72,630	72,960
0.33	67,865	68,700	69,535	70,370	70,655	70,945	71,295	71,670	72,100	72,515	72,930	73,290	73,590	73,890
0.34	68,900	69,760	70,620	71,475	71,705	71,940	72,255	72,655	73,050	73,490	73,925	74,280	74,550	74,820
0.35	69,930	70,815	71,700	72,580	72,755	72,930	73,215	73,610	74,000	74,460	74,920	75,270	75,510	75,750
0.36	70,665	71,530	72,400	73,265	73,545	73,825	74,170	74,590	75,000	75,455	75,910	76,295	76,610	76,920
0.37	71,400	72,250	73,100	73,950	74,335	74,720	75,130	75,565	76,000	76,450	76,905	77,320	77,710	78,090
0.38	72,130	72,965	73,800	74,630	75,120	75,610	76,085	76,545	77,000	77,450	77,895	78,350	78,805	79,260
0.39	72,865	73,685	74,500	75,315	75,910	76,505	77,045	77,520	78,000	78,445	78,890	79,375	79,900	80,430
0.40	73,600	74,400	75,200	76,000	76,700	77,400	78,000	78,500	79,000	79,440	79,880	80,400	81,000	81,600

TABLE 2.—*Steel Works A, Acid Bessemer Steel*

Manganese 0.34 *to* 0.60 *per cent. varying by* 0.02 *per cent.; carbon* 0.10 *to* 0.40 *per cent., varying by* 0.01 *per cent. Average of actual tensile strength of* ¾*-in. round test bars rolled from test ingots.*

Per Cent., Carbon	Per Cent., Manganese													
	0.34	0.36	0.38	0.40	0.42	0.44	0.46	0.48	0.50	0.52	0.54	0.56	0.58	0.60
	Tensile Strength, Pounds per Square Inch													
0.10	64,440	64,480	64,480	64,500	64,600	64,700	64,800	64,900	65,000	65,120	65,240	65,340	65,420	65,500
0.11	64,665	64,695	64,720	64,750	64,900	65,055	65,190	65,310	65,430	65,585	65,740	65,885	66,020	66,150
0.12	64,890	64,930	64,965	65,000	65,205	65,410	65,580	65,720	65,860	66,050	66,245	66,430	66,615	66,800
0.13	65,120	65,160	65,206	65,250	65,505	65,760	65,970	66,130	66,290	66,520	66,745	66,980	67,215	67,450
0.14	65,345	65,395	65,450	65,500	65,810	66,115	66,360	66,540	66,720	66,985	67,250	67,525	67,810	68,100
0.15	65,570	65,630	65,690	65,750	66,110	66,470	66,750	66,950	67,150	67,450	67,750	68,070	68,410	68,750
0.16	66,155	66,245	66,340	66,430	66,810	67,190	67,500	67,735	67,970	68,345	68,720	69,090	69,445	69,800
0.17	66,740	66,860	66,985	67,110	67,510	67,910	68,245	68,520	68,790	69,240	69,695	70,105	70,480	70,850
0.18	67,320	67,480	67,635	67,790	68,210	68,630	68,995	69,300	69,610	70,140	70,665	71,125	71,510	71,900
0.19	67,905	68,095	68,280	68,470	68,910	69,350	69,740	70,085	70,430	71,035	71,640	72,140	72,545	72,950
0.20	68,490	68,710	68,930	69,150	69,610	70,070	70,490	70,870	71,250	71,930	72,610	73,160	73,580	74,000
0.21	69,755	69,975	70,200	70,420	70,900	71,380	71,795	72,145	72,495	73,080	73,665	74,170	74,585	75,000
0.22	71,020	71,245	71,465	71,690	72,190	72,690	73,100	73,420	73,740	74,230	74,725	75,175	75,590	76,000
0.23	72,285	72,510	72,735	72,960	73,480	74,000	74,405	74,690	74,980	75,380	75,780	76,185	76,590	77,000
0.24	73,550	73,780	74,000	74,230	74,770	75,310	75,710	75,965	76,225	76,530	76,840	77,190	77,595	78,000
0.25	74,815	75,045	75,270	75,500	76,060	76,620	77,015	77,240	77,470	77,680	77,895	78,200	78,600	79,000
0.26	75,810	76,075	76,335	76,600	77,100	77,615	77,990	78,230	78,475	78,730	78,990	79,305	79,580	80,050
0.27	76,810	77,110	77,400	77,700	78,155	78,615	78,970	79,225	79,480	79,785	80,090	80,410	80,755	81,100
0.28	77,810	78,140	78,470	78,800	79,205	79,610	79,945	80,215	80,490	80,835	81,185	81,520	81,835	82,150
0.29	78,805	79,170	79,535	79,900	80,250	80,605	80,925	81,210	81,495	81,890	82,285	82,625	82,910	83,200
0.30	79,800	80,200	80,600	81,000	81,300	81,600	81,900	82,200	82,500	82,940	83,380	83,730	83,990	84,250
0.31	80,610	80,990	81,370	81,750	82,050	82,350	82,660	82,980	83,300	83,695	84,090	84,410	84,655	84,900
0.32	81,420	81,780	82,140	82,500	82,800	83,100	83,420	83,760	84,100	84,450	84,805	85,095	85,320	85,550
0.33	82,230	82,570	82,910	83,250	83,550	83,850	84,180	84,540	84,900	85,210	85,515	85,775	85,990	86,200
0.34	83,040	83,360	83,680	84,000	84,300	84,600	84,940	85,320	85,700	85,965	86,230	86,460	86,655	86,850
0.35	83,850	84,150	84,450	84,750	85,050	85,350	85,700	86,100	86,500	86,720	86,940	87,140	87,320	87,500
0.36	85,310	85,610	85,905	86,200	86,505	86,810	87,150	87,525	87,900	88,150	88,395	88,630	88,845	89,060
0.37	86,775	87,065	87,360	87,650	87,960	88,265	88,595	88,950	89,300	89,575	89,850	90,115	90,370	90,620
0.38	88,235	88,525	88,810	89,100	89,410	89,725	90,045	90,370	90,700	91,005	91,310	91,605	91,890	92,180
0.39	89,700	89,980	90,265	90,550	90,865	91,490	91,490	91,195	92,100	92,430	92,765	93,090	93,415	93,740
0.40	91,160	91,440	91,720	92,000	92,320	92,640	92,940	93,220	93,500	93,860	94,220	94,580	94,940	95,300

TABLE 3.—*Comparison of Results of Tensile-strength Tests and Estimated Values of Basic Open-hearth Steel*

Base used for estimated tensile strength for Webster's values 50,145 *lb. per sq. in. for* 0.10 *per cent. carbon and* 0.34 *per cent. manganese. Phosphorus content* 0.02 *per cent. in all cases.*

Per Cent., Carbon	Results	Per Cent., Manganese						
		0.34	0.38	0.42	0.46	0.50	0.54	0.58
		Tensile Strength, Pounds per Square Inch						
0.10	Steel works A.....	50,145	50,950	51,700	52,440	53,000	53,800	54,600
	Estimated.....	50,145	50,825	51,505	52,185	52,865	53,545	54,225
	Difference.....		−125	−195	−255	−135	−255	−375
0.15	Steel works A.....	56,475	56,660	56,800	56,950	57,250	58,010	58,560
	Estimated.....	54,295	54,975	55,655	56,335	57,015	57,695	58,375
	Difference.....	−2,180	−1,685	−1,145	−615	−235	−315	−185
0.20	Steel works A.....	59,300	59,565	59,980	60,570	61,250	62,170	63,030
	Estimated.....	58,445	59,125	59,805	60,485	61,165	61,845	62,525
	Difference.....	−855	−440	−175	−85	−85	−325	−505
0.25	Steel works A.....	61,665	63,120	64,000	64,535	65,200	65,840	66,480
	Estimated.....	62,595	63,275	63,955	64,635	65,315	65,995	66,675
	Difference.....	+930	+155	−45	+100	+115	+155	+195
0.30	Steel works A.....	64,770	66,290	67,510	68,410	69,250	69,945	70,710
	Estimated.....	66,745	67,425	68,105	68,785	69,465	70,145	70,825
	Difference.....	+1,975	+1,235	−595	+375	+215	+200	+115
0.35	Steel works A.....	69,930	71,700	72,755	73,215	74,000	74,920	75,510
	Estimated.....	70,895	71,575	72,255	72,935	73,615	74,295	74,975
	Difference.....	+965	−125	−500	−280	−385	−625	−535
0.40	Steel works A.....	73,600	75,200	76,700	78,000	79,000	79,880	81,000
	Estimated.....	75,045	75,725	76,405	77,085	77,765	78,445	79,125
	Difference.....	+1,445	+525	−295	−915	−1,235	+1,435	−1,875

COMPARISON OF STEEL WORKS *A* TENSION TESTS WITH ESTIMATED STRENGTHS

In order to make a thorough comparison between the methods used by steel works *A* and *X* with the estimated tensile strengths by the methods of Campbell, Cunningham, and Webster, six tables have been prepared, each covering a range of 10,000 lb. (703.08 kg.) in specified tensile strength. Tables 4 to 7 are for steels of about 0.02 per cent. phosphorus and not over 0.031 per cent. Tables 8 and 9, for steels containing 0.06 per cent. phosphorous, are given to bring out clearly the actual increase in tensile strength by the different methods used.

The limits of manganese, 0.34 to 0.56 per cent. inclusive, are much wider than would be used in practice, but they are so made to show more clearly the effect of manganese when used by steel works *A*, Camp-

bell and Webster, and how the tensile strengths arrived at compare with the results of steel works *X* and Cunningham, who do not give it any value.

When taking into consideration all the differences in the six methods used to find the required carbons for tensile strengths called for in the four divisions of the low-phosphorus steels and the two divisions of the higher phosphorus steels, the results agree remarkably well. Any of these methods, by slight modifications to suit the rolling conditions of any mill, could soon be used for the grading of the steel.

These tables were prepared not only for discussion but to induce others to give us similar tables covering their methods used in grading and rolling bessemer steel, basic and acid open-hearth steel and electric steel, also duplex and triplex steels. From a comparison of the methods given for all of these, many important facts would be brought out in the discussion. If any manufacturer does not desire to give full publicity to his methods, they will be submitted to a small committee for a comparison with the other tables and methods given and a short report of its views on same. In this connection, no doubt all of the factors that have a bearing on the quality of the finished steel will be considered and discussed. It is suggested that particular attention be given to the direct or indirect effects of the recarburization of the metal, also to the stock used, etc.

Particular attention is called to the following from A. A. Stevenson's discussion of one of the writer's early papers:[7] "You state that 'the quality of steel depends (1) on its chemical composition; (2) on the treatment it received in the course of manufacture.' I would go a step further and say that, in my opinion, as far as open-hearth steel is concerned, the physical results, to a certain extent, depend on manipulation of the bath in the furnace.

"Concerning the relations between the chemical composition and physical results, I must say I have been somewhat surprised to find how close this relation is. The point in question has been brought out strongly in test work we have recently done on some tires made for a foreign government to a rather difficult specification."

His remarks on the importance of the treatment of steel in the furnace were considerably ahead of the times, but have been fully confirmed since then, and recently it has been found that variations in the working of the blast furnace at times produce undesirable conditions that carry through all the way to the finished steel. The conditions referred to are no doubt due to oxygen in the steel, and it is to be hoped that we will have a full discussion on this question.

Underlying this whole matter are the changes in the structure of steel

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[7] *Jnl.* Fraaklin Inst. (January, 1899) **147**, 14.

TABLE 4.—*Carbon Limits* for Basic Open-hearth Steel 7/16 in. Thick; Desired Rolling Limits about 52,000–58,000 lb.*

Phosphorus content 0.02 per cent.; specified ultimate strength 50,000–60,000 lb.

	Low Limit			High Limit		
	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch
Steel works A	0.12	0.34	52,675	0.15	0.34	56,475
	0.12	0.56	55,850	0.15	0.56	58,320
Campbell	0.12	0.34	52,346	0.15	0.34	55,496
	0.12	0.56	54,210	0.15	0.56	57,360
Webster	0.09	0.34	52,220	0.12	0.34	55,020
	0.09	0.56	55,100	0.12	0.56	57,900
Cunningham	0.10	0.34	52,000	0.16	0.34	58,000
	0.10	0.56	52,000	0.16	0.56	58,000
Steel works X	0.11	0.34	52,000	0.16	0.34	58,000
	0.11	0.56	52,000	0.16	0.56	58,000
Estimated tensile strengths by	0.12	0.34	51,805	0.15	0.34	54,295
Webster. (See Table 3.)	0.12	0.56	55,545	0.15	0.56	58,035

TABLE 5.—*Carbon Limits* for Basic Open-hearth Steel 7/16 in. Thick; Desired Rolling Limits about 62,000–68,000 lb.*

Phosphorus content 0.02 per cent.; specified ultimate strength 60,000–70,000 lb.

	Low Limit			High Limit		
	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch
Steel works A	0.25	0.34	61,665	0.27	0.34	62,905
	0.25	0.56	66,160	0.27	0.56	67,820
Campbell	0.21	0.34	61,796	0.25	0.34	66,002
	0.21	0.56	63,660	0.25	0.56	67,866
Webster	0.20	0.34	62,020	0.24	0.34	65,220
	0.20	0.56	64,900	0.24	0.56	68,100
Cunningham	0.20	0.34	62,000	0.26	0.34	68,000
	0.20	0.56	62,000	0.26	0.56	68,000
Steel works X	0.21	0.34	62,000	0.26	0.34	68,000
	0.21	0.56	62,000	0.26	0.56	68,000
Estimated tensile strengths by	0.24	0.34	61,765	0.27	0.34	64,255
Webster. (See Table 3.)	0.24	0.56	65,505	0.27	0.56	67,995

* Carbon limits vary with material rolled and conditions of rolling at different mills.

TABLE 6.—*Carbon Limits* for Basic Open-hearth Steel 7/16 in. Thick; Desired Rolling Limits about 57,000–63,000 lb.*

Phosphorus content 0.02 per cent.; specified ultimate strength 55,000–65,000 lb.

	Low Limit			High Limit		
	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch
Steel works A	0.16	0.34	57,040	0.20	0.34	59,300
	0.16	0.56	59,180	0.20	0.56	62,610
Campbell	0.16	0.34	56,546	0.20	0.34	60,746
	0.16	0.56	58,410	0.20	0.56	62,610
Webster	0.14	0.34	57,020	0.18	0.34	60,420
	0.14	0.56	59,900	0.18	0.56	63,300
Cunningham	0.15	0.34	57,000	0.21	0.34	63,000
	0.15	0.56	57,000	0.21	0.56	63,000
Steel works X	0.16	0.34	57,000	0.22	0.34	63,000
	0.16	0.56	57,000	0.22	0.56	63,000
Estimated tensile strengths by Webster. (See Table 3.)	0.18	0.34	58,785	0.21	0.34	59,275
	0.18	0.56	60,523	0.21	0.56	63,015

TABLE 7.—*Carbon Limits* for Basic Open-hearth Steel 7/16 in. Thick; Desired Rolling Limits about 67,000–73,000 lb.*

Phosphorus content 0.02 per cent.; specified ultimate strength 65,000–75,000 lb.

	Low Limit			High Limit		
	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch
Steel works A	0.32	0.34	66,835	0.33	0.34	67,865
	0.32	0.56	72,295	0.33	0.56	73,290
Campbell	0.26	0.34	67,046	0.30	0.34	71,246
	0.26	0.56	68,910	0.30	0.56	73,110
Webster	0.26	0.34	66,820	0.30	0.34	70,020
	0.26	0.56	69,700	0.30	0.56	72,900
Cunningham	0.25	0.34	67,000	0.31	0.34	73,000
	0.25	0.56	67,000	0.31	0.56	73,000
Steel works X	0.26	0.34	67,000	0.31	0.34	73,000
	0.26	0.56	67,000	0.31	0.56	73,000
Estimated tensile strengths by Webster. (See Table 3.)	0.30	0.34	66,745	0.33	0.34	69,235
	0.30	0.56	70,485	0.33	0.56	72,975

* Carbon limits vary with material rolled and conditions of rolling at different mills.

TABLE 8.—*Carbon Limits* for Basic Open-hearth Steel 7/16 in. Thick; Desired Rolling Limits about 57,000–63,000 lb.*

Phosphorus content 0.06 per cent.; specified ultimate strength 55,000–65,000 lb.

	Low Limit			High Limit		
	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch
Steel works A	0.12	0.34	56,675	0.15	0.34	60,475
	0.12	0.56	59,850	0.15	0.56	62,320
Campbell	0.12	0.34	56,546	0.16	0.34	60,746
	0.12	0.56	58,416	0.16	0.56	62,610
Webster	0.10	0.34	57,020	0.13	0.34	60,020
	0.10	0.56	59,900	0.13	0.56	62,900
Cunningham	0.11	0.34	57,000	0.17	0.34	63,000
	0.11	0.56	57,000	0.17	0.56	63,000
Steel works X	0.10	0.34	57,000	0.16	0.34	63,000
	0.10	0.56	57,000	0.16	0.56	63,000
Estimated tensile strengths by Webster. (See Table 3.)	0.13	0.34	56,635	0.16	0.34	59,125
	0.13	0.56	60,375	0.16	0.56	62,875

TABLE 9.—*Carbon Limits* for Basic Open-hearth Steel 7/16 in. Thick; Desired Rolling Limits about 67,000–73,000 lb.*

Phosphorus content 0.06 per cent.; specified ultimate strength 65,000–75,000 lb.

	Low Limit			High Limit		
	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch	Per Cent. Carbon	Per Cent. Manganese	Ultimate Strength, Pounds per Square Inch
Steel works A	0.27	0.34	66,905	0.28	0.34	67,530
	0.27	0.56	71,820	0.28	0.56	72,655
Campbell	0.22	0.34	67,046	0.26	0.34	71,246
	0.22	0.56	68,910	0.26	0.56	73,110
Webster	0.21	0.34	66,820	0.25	0.34	70,020
	0.21	0.56	69,700	0.25	0.56	72,900
Cunningham	0.21	0.34	67,000	0.27	0.34	73,000
	0.21	0.56	67,000	0.27	0.56	73,000
Steel works X	0.20	0.34	67,000	0.25	0.34	73,000
	0.20	0.56	67,000	0.25	0.56	73,000
Estimated tensile strengths by Webster. (See Table 3.)	0.25	0.34	66,595	0.28	0.34	69,085
	0.25	0.56	70,335	0.28	0.56	72,825

* Carbon limits vary with material rolled and conditions of rolling at different mills.

produced by the heat treatment and work it receives in rolling. These changes are recognized in the ordinary fractures and in some cases in the polished and etched surfaces without the use of a glass. Low-power hand glasses have been used to advantage, but there is yet a wide and promising field of microscopical research work on low-carbon structural steel.

In 1894, the writer first called attention to this important point and endeavored to show that at times the chemical composition of steel was of less importance than the poor structure due to improper treatment in heating and rolling. His remarks were in part as follows:[8]

"When rolling heavy steel plates, trouble is often caused by finishing them at too high a temperature, which gives a material with crystalline fracture, poor reduction of area, and poor bends. In order to guard against this and control the finishing temperature we use very light drafts in rolling, and produce as good results in heavy plates as in the light ones. Too much importance cannot be given to the heat treatment of steel."

The writer in 1904 in a discussion of Mr. Campbell's paper said:[9]

"I agree with Mr. Campbell in that it is not necessary to take the microstructure of the steel into consideration from the standpoint of his investigation. Yet anything that will in any way assist in controlling the heat treatment of the steel should be looked into. In the ordinary microscopical work they have not tied up the fractures of a nicked and broken piece of steel, as we know it, with the microstructure of the same steel. This step from the old to the new has long been needed, and I now desire to call attention to a method of slight etching and low magnification with a hand-glass that is very promising. It looks as though by this method we will be able to tie up the fractures of steel of, say, 0.50 carbon and under. These pieces are from the same bar of 0.35 carbon acid open-hearth steel. One piece was overheated and shows the large coarse structure; the other piece was overheated and then annealed; it shows a much finer structure. A test of this kind would be useful in the case of large driving axles, as a small spot could be polished and etched; the glass would show if the steel had been finished at too high a temperature in forging; that is, if it had too large a grain and was in a dangerous condition. This method of investigation is offered at this time as a suggestion in the hopes that others will take it up and improve it."

The first practical use in examining large forgings as suggested above was by Col. W. P. Barba during the war, and he has kindly given me the following information regarding this work:

"During 1917, Wm. R. Webster, in conversation with me, showed

[8] *Jnl.* Iron and Steel Inst. (I, 1894) **45**, 335.
[9] *Jnl.* Iron and Steel Inst. (II, 1904) **66**, 65.

that in his practice, he had recognized a need which we had but recently developed in our field work, in production of high-quality forgings for war purposes. This need was to discover on polished surfaces, the nature and extent, as well as the probable seriousness of solid non-metallic inclusions which had come to light on finished surfaces during manufacture.

"Mr. Webster then contributed to the service of the Government, through me, a small portable microscope, working to approximately 50 diameters (?), and which could easily be dismounted and packed in a grip, carried to any location in the field, and readily set up on a large forging under examination, and proved its great usefulness in determining the seriousness of such inclusions in a manner which in no way interfered with the future usefulness of the piece.

"Some such apparatus as that which was provided by Mr. Webster, out of his large experience, would be of great use if much more extensively applied in practical inspection and works-control operations."

No paper of this kind would be complete without referring to Doctor Howe's views on the effect of carbon on the ultimate strength of steel, given in "Metallurgy of Steel" in 1892, and without trying to solve the problem he gave at that time. For several years this problem appeared difficult to the writer, but the advances in metallurgy of steel since 1892 have practically solved it. The tables of averages of the ¾-in. round tests of steel works *A* more than cover the wide limits for carbons under 0.40 per cent., without taking into account the changes in tensile strength due to thickness of material rolled, and the varying limits of carbon found necessary to secure the same tensile strength in all thicknesses of material rolled from the same heat of steel. While not used, this greatly simplified the problem. Doctor Howe in "Metallurgy of Steel" states: "While we cannot accurately qualify the effects of carbon, I believe that for ordinary unhardened merchantable steel, the tensile strength is likely to lie between the following pretty wide limits:

Carbon, Per Cent.	Lower Limit	Upper Limit	Differences by Webster
0.05	50,000	66,000	16,000
0.10	50,000	70,000	20,000
0.15	55,000	75,000	20,000
0.20	60,000	80,000	20,000
0.30	65,000	90,000	25,000
0.40	70,000	100,000	30,000
0.50	75,000	110,000	35,000
0.60	80,000	120,000	40,000
0.80	90,000	150,000	60,000
1.00	90,000	170,000	80,000
1.30	90,000	115,000	25,000

For the consideration of these limits to be expected in the lower carbons from 0.05 to 0.40 per cent. carbon inclusive, the upper and lower limits have been subdivided as shown in Table 10 (Howe), in which is given a subdivision of these limits from 0.05 to 0.40 per cent. carbon, inclusive. The second column gives the lower limits and the last column gives the upper limits. The third column is one-quarter of the difference of increase between the upper and lower limits; the fourth column is one-half of this increase; and the fifth column three-quarters of the increase. The upper and lower limits for 0.25 per cent. carbon and 0.35 per cent. carbon have been added to the limits given by Doctor Howe for convenience of investigation; they are merely the limits between the values that he gives for 0.20, 0.30 and 0.40 per cent. carbon. At the foot of each column is given the average effect of 0.01 per cent. carbon.

TABLE 10.—*Effects of Carbon on Tensile Strength, According to Howe*

Per Cent., Carbon	Lower Limit, Pounds per Square Inch	One-Quarter Increase, Pounds per Square Inch	One-Half Increase, Pounds per Square Inch	Three-Quarters Increase, Pounds per Square Inch	Upper Limit, Pounds per Square Inch
0.05	50,000	54,000	58,000	62,000	66,000
0.10	50,000	55,000	60,000	65,000	70,000
0.15	55,000	60,000	65,000	70,000	75,000
0.20	60,000	65,000	70,000	75,000	80,000
0.25	62,500	68,000	73,750	79,375	85,000
0.30	65,000	71,250	77,700	83,750	90,000
0.35	67,500	74,375	81,520	88,125	95,000
0.40	70,000	77,500	85,000	92,500	100,000
Effect of 0.01 per cent., carbon....	666	750	833	917	1,000

In Table 11 are given the nearest values of steel works *A* corresponding to the subdivisions of Doctor Howe's values. These values are given with an increase of two points of phosphorus from 0.02 to 0.08 per cent. in basic open-hearth steel; the last column is for bessemer steel containing 0.10 per cent. phosphorus. As their tables do not give 0.05 per cent. carbon, this table starts with 0.10 per cent. carbon. The average effects for 0.01 per cent. carbon are given at the bottom of each column.

It is unreasonable to expect that the values of carbon and other elements that apply to the lower steels can be applied equally well to the higher steel, as the difficulties in meeting the requirements of specifications increase as the tensile strength increases. This is due to reductions in rolling and finishing temperature having a greater effect on the higher carbon steels. An exception to this was shown about

TABLE 11.—*Effects of Carbon on Tensile Strength, According to Steel Works A*

Per Cent. Carbon	Tensile Strength, in Pounds per Square Inch, with				
	P 0.02% Mn 0.34%	P 0.04% Mn 0.50%	P 0.06% Mn 0.72%	P 0.08% Mn 0.80%	P 0.10% Mn 0.94%
0.10	50,140	55,000	60,090	63,000	69,540
0.15	56,475	59,250	65,200	68,000	75,080
0.20	59,300	63,250	69,400	72,700	81,820
0.25	61,665	67,200	72,950	77,770	85,600
0.30	64,770	71,250	78,400	82,000	89,960
0.35	69,930	76,000	82,450	86,000	93,460
0.40	73,600	81,000	89,460	93,000	100,160
Effect of 0.01 per cent., carbon....	782	866	979	1,000	1,054

twenty years ago by A. A. Stevenson, then manager of the Standard Steel Works, who had been interested in the writer's work. He rolled successfully several export orders of locomotive tires, subject to both tension and deflection tests, from heats of acid open-hearth steel graded from their chemical composition by Webster's values. He paid great attention to the reductions in rolling and finishing temperatures of these tires, which met perfectly all the tension and deflection tests called for by the specifications on the unannealed tires. This showed that where all the rolling conditions could be controlled the relation between the chemical composition and mechanical properties could be relied on for steels considerably higher in tensile strength and carbon than the usual structural steel.

The results given and the comparisons made in Tables 10, 11 and 12, with other data given, put the relation between the chemical composition of steel and its physical properties on a much firmer basis than formerly when carbon alone was expected to account for practically all of the differences in the tensile strength of steel.

For convenience of comparison, in Table 12 the two tables are combined, Howe's values being given on the upper lines and steel works *A* on the lower lines in each subdivision. The results are much closer than was to be expected and is a step toward the solution of the problem given by Doctor Howe in 1892.

Table 12 shows that the average effect of 0.01 per cent. carbon from 0.10 to 0.40 per cent. increases with the increase of phosphorus and manganese.

TABLE 12.—*Comparison of Results Obtained by Howe and Steel Works A*

	Per Cent. Carbon	Tensile Strength, Pounds per Square Inch, with				
		P 0.02% Mn 0.34%	P 0.04% Mn 0.50%	P 0.06% Mn 0.72%	P 0.08% Mn 0.80%	P 0.10% Mn 0.94%
Howe	0.05	50,000	54,000	58,000	62,000	66,000
Steel works A						
Howe	0.10	50,000	55,000	60,000	65,000	70,000
Steel works A	0.10	50,140	55,000	60,090	63,000	69,540
Howe	0.15	55,000	60,000	65,000	70,000	75,000
Steel works A	0.15	56,475	59,250	65,200	68,000	75,080
Howe	0.20	60,000	65,000	70,000	75,000	80,000
Steel works A	0.20	59,300	63,250	69,400	72,700	81,820
Howe	0.25	62,500	68,000	73,750	79,375	85,000
Steel works A	0.25	61,665	67,200	72,950	77,700	85,600
Howe	0.30	65,000	71,250	77,700	83,750	90,000
Steel works A	0.30	64,770	71,250	78,400	82,000	89,960
Howe	0.35	67,500	74,375	81,520	88,125	95,000
Steel works A	0.35	69,930	76,000	82,450	86,000	93,460
Howe	0.40	70,000	77,500	85,000	92,500	100,000
Steel works A	0.40	73,600	81,000	89,460	93,000	100,160
Average effect of 0.01 per cent. carbon.						
Howe		666	750	833	917	1,000
Steel works A		782	866	979	1,000	1,054

APPENDIX *

We can look with great satisfaction on what has been accomplished by the Institute through the papers and discussions on the physics of steel, starting in 1893 and extending over several years, which paved the way for the general movement on standardization that was taken up, a few years later, by other societies. The work of the Institute was carried on by individual members, as committee work was not encouraged until recent years, but Doctor Raymond always kept the Institute in close touch with the important standardization work being done by committees of other societies, especially those working on the specifications for iron and steel, by having their specifications presented at our

* Presented at meeting with summary of paper.

meetings for discussion. This brought the American Society for Testing Materials in very close touch with our Institute. Both societies were always glad to coöperate and have all metallurgical matters discussed in this way, neither society encroaching upon the work of the other, and both were benefited and greatly indebted to Doctor Raymond for his course of procedure.

The American Society for Testing Materials has always been the natural clearing house for specifications for iron and steel, and will continue to be. Its work was successful from the start, largely because manufacturers and consumers of steel were given an equal representation and vote on all matters dealing with these specifications. In addition, the society coöperated with the committees of other societies dealing with similar specifications and endeavored to harmonize the specifications wherever possible.

The satisfactory results of the A. S. T. M.'s work naturally had considerable influence in bringing about the organization of the American Engineering Standards Committee, about four years ago, by the four national engineering societies and the American Society for Testing Materials. Since then five departments of the Government [Commerce (Bureau of Standards), War, Navy, Interior, Agriculture] and several other bodies have joined, including the Society of Automotive Engineers, the American Railway Engineering Association, and the American Steel Manufacturers Association.

The American Engineering Standards Committee is doing a great work in harmonizing the standards and standard specifications now in use. On the approval of any standard by the main committee, it becomes an "American standard," a "tentative standard" or a "recommended practice" according to circumstances and nature of the standard. After approval by the main committee, the standard is published by the sponsor under appropriate title, and over the statement "approved by the American Engineering Standards Committee." These American standard specifications will undoubtedly come into general use for both home and export orders.

The Institute, as one of the founder members of the American Engineering Standards Committee, must do its share of this important work and a most promising field for this is offered by our new discussion on the physics of steel. The field covered by this discussion will be wide enough to take in all of the important requirements of our present specifications and bring up to date several matters that are much better understood than when some of these specifications were adopted. This course will greatly assist in harmonizing the slight differences in a few of the specifications in general use before a single one for each grade of steel can be agreed on for submission to the committee for adoption as an American standard specification.

I have endeavored to show how, in every day rolling-mill work, the practical use of the relations between the chemical composition of steel and its physical properties is giving satisfactory results. Formerly it was claimed that this could not be done, but now this use is so general that no one thinks of it or the immense saving in cost of manufacture by rolling much of the steel without letting it lose the original heat of casting, thus avoiding the former reheatings and saving a large tonnage of coal.

While these results are most satisfactory, they can be much improved if we get the coöperation of the manufacturers of all makes of steel now used, as up to the present, too much has been expected from the results obtained from steel manufactured by one method when they are applied to steel manufactured by other methods. It is only by concentrating upon the different methods in use at several steel works that new information can be obtained. The data should include the limits of carbon, phosphorus, and manganese for the five or six grades of structural steel, with the variations in carbon allowed for the thickness of the material rolled. Many full tables of this kind are in general use at different mills and a comparison of them would greatly assist in this work.

The following matters are offered for discussion as they have an important bearing on the standardization of steel specifications and the physics of steel. Up-to-date information on these subjects is requested from both producers and consumers of steel in order that each may be intelligently discussed and decided on its merits. Then, should it be found necessary, modifications can be made in or additional check tests embodied in the proposed American Standard Specifications. This course, for the Institute, is practically the same as it followed with the A. S. T. M., only now it covers a much wider and more important field.

Undesirable Dirty Steel

During the rush of work in recent war times, it was found that steel manufacturers in some parts of the country could not work to the carbon limits specified and meet the physical tests called for, while manufacturers in other localities had no difficulty in complying with both requirements. In the former case, concessions were asked and claims made that the carbon limits would have to be increased considerably, in order that the steel would meet the physical tests; these concessions were granted in order to get the steel needed. On investigation, it was found that the former mills were making a dirty steel, thus causing the trouble, and that the latter mills were making a good clean steel. As there is now no great demand for steel it would seem that this is a good time to discuss this subject thoroughly in order that a simple clause can be agreed upon and added to our specifications and in that way exclude the use of dirty steel in the future.

Minimum Limit of Manganese

Considerable trouble has been experienced in flanging boiler plates that had complied with all the chemical requirements and physical tests of several specifications for flange plates. This trouble was not due to improper heating or careless work in flanging, as plates from other heats of steel that were heated and flanged by the same men at the same time gave satisfactory results. On investigation the trouble was found to be caused by low manganese, it being considerably under 0.30 per cent. Sufficient data can be produced to show the necessity of having a minimum limit for manganese embodied in all specifications for flange steel.

Heat Treatment of Steel by Work in Rolling or Forging

More trouble is found in working the thicker steel plates and heavier weights of rolled sections than with the medium weights and sections. This is due to two causes: First, finishing the rolling at too high a temperature and not making sufficient check tests of the thickest plates or sections rolled. Or, where both cold and quench bends are called for, often only the quench bends are made, which are worse than useless, as the steel is annealed by the heating and the carbon is not high enough in ordinary structural steel to harden it in quenching. Yet, this heavy steel will not bend cold in the condition as rolled, though it will often give good elongation and reduction of area.

Second, too heavy reductions in the first passes of rolling, sufficient to bring out what is often called the "second heat in rolling," causes the steel rolled or forged to look hotter than when it was drawn from the furnace, and it makes no difference how light the finishing work in rolling or forging may be, or how low the finishing temperature, the finished material is unreliable.

The grain growth of the steel by heating for rolling or forging, can only be reduced and broken by sufficient work at low temperatures which could not be put upon it in either of the conditions referred to.

This subject is important and considerable useful information can be gained from a full discussion of the changes in the structure of the heavy steel, and methods developed that will assist in avoiding these troubles. Many of the so-called mysterious failures of steel have been caused by material of this kind getting into service.

Use and Advantages of Proof Tests

Proof tests are those that can be made on the article during manufacture or in its finished condition without injury to its usefulness. We are all familiar with tests of this kind and their general use in many kinds of steel work. A new field is the development of what may properly be called a proof test of the grain structure of the finished article or a check

test on it during manufacture. This test is by polishing a small surface and examining it with a hand magnifying glass, as referred to, or with a portable microscope, as explained and endorsed by Colonel Barba. Such examinations on locomotive driving axles, or other large forgings, that have failed in service will, in practically all cases, show the large coarse-grained steel that cause the failure.

As a check on new forgings, it would only be necessary to examine a few from each turn's work, in order to check up the structure of the steel in the finished forgings. The value of this method of inspection cannot be fully appreciated until it has been given a fair trial.

DISCUSSION

GEORGE B. WATERHOUSE,* Buffalo, N. Y.—Most of our steels must meet physical specifications, and all our steel is made from a chemical basis, so that we have a formula similar to that worked out in this paper. It is not quite the same, however, and we will be pleased to give the author what records and information we have on this subject.

J. O. LIEBIG,† Lancaster, Pa.—I would like to see compiled data covering the commercial sizes of material, the yield points, tensile strength, reduction of area, etc., considering each S. A. E. specification, giving the corresponding physical properties for those specifications, that data to be gotten in the hot-rolled condition. After we gathered that in the hot-rolled condition, we could get the data in the cold-drawn condition of materials. This, I believe, would be very useful, although I have not seen any data compiled along these lines.

RALPH H. SWEETSER,‡ Columbus, Ohio.—Many times, steel makers complain of the pig iron, when there has been trouble in the rolling of the steel, yet an analysis for phosphorus, manganese, carbon, and sulfur will show the same content as in iron which has been satisfactory. Sometimes the steel men say that "oxide of iron" is present in such a way in the pig iron, that it can never be removed; I do not know anything about it, but I would suggest that together with the points brought up by the author, that the question of the oxide of iron in pig iron be investigated. It may furnish some information regarding dirty steel.

H. T. MORRIS,§ Bethlehem, Pa.—Some persons seem to think that when steel of a given composition fails to show certain expected physical properties, that the steel is dirty. Such a conclusion is not at all warranted. For various reasons, the analysis of a piece of steel in one labora-

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† Metallurgist, Lancaster Steel Products Co.

‡ Assistant to Vice-president, American Rolling Mill Co.

§ Metallurgical Engineer, Bethlehem Steel Co.

tory may not agree with the analysis of that same piece of steel in another laboratory. But even in cases where the analyses check reasonably well a piece of steel made in our plant, for instance, will not give the same physical results as a piece of steel made in some other plant, though of the same composition. This is accounted for by a number of conditions that are different in any two mills; also by differences in location of test bars, their condition when pulled (scratches, notches, etc.), methods of pulling, etc.

The contention of those manufacturers who insist that physical properties be specified and not chemical properties, at least not so far as carbon is concerned, as against specifying both chemical and physical properties, is perfectly sound. It does not mean that the manufacturer who objects to having both analysis and physical properties specified is trying to hide dirty steel, or anything of that kind.

With reference to the formulas for analyses so as to produce certain physical results, most of us are aware that the American Society for Steel Treating and the Society of Automotive Engineers are developing a set of charts for a great number of grades of steels, both carbon and alloy, in which the physical properties are shown for a given range of compositions and for given methods of a heat treatment. Our company has collaborated substantially in this work.

The microscope tells us many things, but while the microscope is used a good deal in the Bethlehem plant, I sometimes think that microscopists have not always proved the assertions they have made. We have a great deal to learn before we can say that certain microscopic evidence means such and such things; it might mean something else.

F. D. CARNEY, New York, N. Y.—As far as the minimum content of manganese in soft structural steel is concerned, it is possible by the churning or rimming method to make steel of good working qualities as low as 0.20 per cent. I was associated with H. H. Campbell, general manager of the Pennsylvania Steel Co., when he worked out his formula to determine the tensile strength of steel from its chemical analyses. This work was done two years after Mr. Webster's observations at the Pottstown Iron Works.

We assembled groups of test bars with carbon worked by the combustion method for this work. The test bars were made from 6-in. ingots. The bottom half was forged to a 2 in. square billet, then rolled to a 2 by ⅜ in. flat, cooled under uniform conditions, and tested for physical qualities. The values we obtained for the various elements were a fair check of physical qualities, but in practical operations for 30 years, working all sections and thicknesses of structural steel and plates, we found the physical results obtained from test bars from a 6-in. ingot rolled to 2 by ⅜ in. flat to be a more reliable method of grading steel into the

8000-lb. limit of structural steel specifications than the use of any chemical formula.

W. P. BARBA, Philadelphia, Pa.—The portable microscope was rather widely used by Mr. Tassin, for some time attached to the Washington Navy Yard, for the development of suspected spots along the surface of materials that could not be tested without the destruction of much that was of great value. Gun forgings, for example, can be tested only at the ends; they can be put under the ordinary microscopic development only at the ends. The Tassin microscope was used for the examination of suspected spots along the surface of the forging, which might be 60 ft. long.

When, however, the microscope is applied to the surface examination of structural or merchant materials, which are much more susceptible to complete examination and determination of their structural values than the special forgings to which I have referred, the value of the portable microscope diminishes. Many of us have worn out one eye looking through a microscope, but it took many thousands of observations, records, and photographs before we began to relate the incidence of the various occurrences that the microscope showed. As has been said, it tells a lot of things that we do not know about, also a lot of things that we know about. It is the finiteness of the human understanding and knowledge of natural things that puts this limitation upon us.

I want to second the author's request for additional information along the lines developed in his paper. I am just as certain that good will come out of it as I am that good has come out of the use of the microscope for research development and daily manufacturing control purposes and uses.

In a discussion of this kind we must take into consideration the kind of steel being made and the plant making it. There are places where highly refined killed steel is made. Dirt is a comprehensive term; it can be chemical dirt or it can be mechanical dirt. It is impossible to say that a steel is dirty; that is purely a comparative term. It is necessary to define closely whether mechanical or chemical dirt is meant before it is possible to decide whether a steel is comparatively clean or comparatively dirty. Again, the use to which steel is to be put determines the amount of cleanness that is required.

There are in this country the brains and the ability to make as good steel in America, from American materials, and following American practice, as can be bought anywhere in the world. It is in no sense necessary to import steel into America to get quality.

JOHN H. NELSON,* Worcester, Mass.—We use in the manufacture of automobile crankshafts 0.40 to 0.50 per cent. carbon steel. During the past year, we made a careful study of our heat-treating records (the

* Metallurgist and Research Engineer, Wyman-Gordon Co.

result was given at the annual meeting of the Society of Automotive Engineers, January, 1922) covering 109 melts of steel, purchased from various mills, and believed to be fairly representative of their best product in this grade. The specifications by which these steels were purchased called for 0.40 to 0.50 per cent. carbon, 0.60 to 0.80 per cent. manganese, and the usual limits on phosphorus and sulfur; all of the melts were within these limits. The physical requirements of the steel, when properly heat treated, are: yield point, minimum, 70,000 lb. per sq. in.; tensile strength, 100,000 lb. per sq. in.; elongation 18 per cent.; contraction, 50 per cent.; with 228 to 248 Brinell hardness.

In compiling the records for this study, these steels were classified in groups according to the drawing temperatures required to meet these physical specifications. After these had been grouped and an average of the chemical composition as well as the physical properties had been taken, it was found that the average carbon contents of these various groups did not vary by more than approximately four points, with a manganese variation of approximately six points, high and low carbon and high and low manganese being found in all the groups. The physical properties obtained after heat treatment gave a variation of not over 5000 lb. per sq. in. on the yield point, with 6000 lb. per sq. in. on the tensile strength on an average of approximately 1100 tests.

The drawing temperatures used to produce these physical properties was varied from 980° to 1120° F. so that in heat-treated materials we have another variable to contend with, namely, drawing temperatures. It is therefore questionable whether any formula can be worked out on chemical composition alone that will give, with any degree of accuracy, the physical properties that may be expected.

Our experience has been that it is absolutely necessary to treat every melt of steel as a separate unit. We therefore segregate all our steels by heat numbers, both in the stock yard and throughout the entire process of manufacture, in order that we may be able to specify with some degree of accuracy the heat treatment necessary to meet definite physical specifications.

GEORGE K. BURGESS,* Washington, D. C.—It would be unsatisfactory to consider manganese content alone; in view of the fact that manganese and sulfur are, within certain limits, always associated we should preferably speak of the manganese-sulfur ratio. In other words, a lower manganese content might be associated with low sulfur than with high sulfur.

As to the development of formulas relating the chemical constituents to the physical properties of the types of steel treated of by the author, at my request Dr. R. W. Woodward, of the Bureau, made an attempt to

*Chief, Division of Metallurgy, Bureau of Standards.

develop such formulas by least squares. These data, however, do not appear to lend themselves adequately to a least-square treatment and this mathematical examination confirmed what has been said here this morning: There are many more variables than appear on the surface.

The chemistry, as given, is so locked up with the history of the steel and its treatment, both thermal and mechanical, that in the finished product, although there is an apparently definite chemical composition and as definite physical properties, passing from one heat of steel to another it appears to be unsafe, except as a rough approximation, to use such a formula.

A phase of the chemistry of steel with which this paper does not treat, but which has undoubtedly a great influence on the final properties of steel, is the gas content of the steel. The gas content of various heats of steel may be very different; their effects are as yet uncertain and hidden, and unquestionably contribute to the final properties of the steel in ways we do not know at the present time. Considerable research work along this line, however, is being pursued at the Bureau of Standards and elsewhere.

It is highly desirable to have suitable adequate temperature control of the most important operations in the manufacture of steel, as pointed out by the author, and there are available satisfactory pyrometers for determining and controlling both the finishing temperatures and the temperatures of the liquid metal. The idea that was prevalent a few years ago, that it was sufficient to use the pyrometer in the finishing or melting shop without intelligent control is passing away; just as the successful use of the microscope in metallography depends on the brain behind the eye, so the results obtained with the pyrometer depend on the operator for neither the microscope nor the pyrometer thinks.

WILLIAM R. WEBSTER (author's reply to discussion).—In the discussion a large part of the steel business was covered, and great interest taken in the subjects brought up. I thank all who took part in this discussion and especially Mr. Stevenson, who presented the paper. Several of the most important matters discussed have been so fully covered in the paper of Doctor Howe and Colonel Barba, and that of Mr. Priestly that there is little left for me to add.

Colonel Barba fully answered Mr. Morris' comments on the use of the microscope. He has also answered questions regarding variation in the steel made at different plants, and took an active part in the discussion of other important matters that were brought up. I thank him for this, and for seconding the request for additional information along the lines developed in the paper. His optimistic views on these subjects are most encouraging.

We all agree with, and endorse, the following conclusion[10] to his

[10] See page 244.

remarks, on the ability of our steel manufacturers to meet all the demands that can be made on them for good reliable steel:

> There are in this country the brains and the ability to make as good steel in America from American materials, and following American practice, as can be bought anywhere in the world. It is in no sense necessary to import steel into America to get quality.

I thank Doctor Burgess for calling attention to the failure to refer to the great effect that the "gas content of the steel has on the final properties of the steel." I have always fully appreciated this important matter, and referred to it in a paper read before the Iron and Steel Institute, in 1894, as follows:[11]

> When it was suggested that I should bring the results of my investigation before the Iron and Steel Institute, I hesitated about doing so until they were in a more complete form, including a full investigation of the effects of silicon and of the gases; but as this may require several years more work, I concluded to present the results in their present form, in hopes that they will be fully criticised, and that there will be found enough new matter in them to induce others to take up or continue the work in this important line of investigation.

Sir Robert Hadfield, in the discussion, referred to the papers of Professor Arnold on The Physical Influence of Elements upon Iron and of W. Galbraith, On the Presence and Influence of Oxides in Iron and Steel, he said:

> In the above cases, where referring to the remelted material, there should be little or no disturbing condition as regards occluded gases, the remelted samples having been prepared in the crucible and out of actual contact with the gases of combustion. They should, therefore, be less influenced in that respect than if produced by other fusion processes. That we specially referred to in face of the remark by the author as to the effect of oxygen.
>
> As regards the effect of oxygen, the question arose whether that element could exist free and alone in iron? Having little or no data, it was not safe to make strong statements as to this; but did it not seem more probable that that element could not exist except in combination? It was known how powerfully it acted on iron if the latter was introduced into it in a finally divided state. Would not that action be even more marked at high temperature? It would be of special interest to determine that before coming to a definite conclusion, though A. Lantz, of the Peine Works, Germany, in a private communication, stated that he considered that element had a marked effect by increasing the tenacity of iron nearly one-half ton per square inch, at the same time reducing its ductility. Professor Ledebur had, he believed, contributed some investigations on this subject. The question of the presence of this element as free or in combination as a special oxide was referred to, as it might have an important bearing on the work which Mr. Webster had in hand. Quite recently there came before the Sheffield Metallurgical Society an interesting paper by W. Galbraith On the Presence and Influences of Oxides in Iron and Steel. That gentleman considered that there was a lower oxide which, when present, had considerable influence upon the mechanical and physical properties of steel.

Both of the papers referred to are worthy of careful consideration at this time.

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[11] *Jnl.* Iron and Steel Inst. (No. 1, 1894) 328.

It is to be hoped that Doctor Burgess, of the Bureau of Standards, and Dr. F. C. Langenberg, metallurgist, Watertown Arsenal, will soon develop, by their research work, methods by which they can determine the gases and the character of the oxides existing in the steel, and thus assist the manufacturers in overcoming the many difficulties that are now met with from these causes in the manufacture of steel, starting with the metal from the blast furnace and continuing all the way through to the finished rolled product. The manufacturers know, in a general way, the cause of some of their troubles, and how to overcome them, but this is not enough, and the proper solution of them will only be reached as I suggest above.

Doctor Burgess has given us the following statement of some of the difficulties met when grading steel from its chemical composition. He might also have referred to the change of structure in the steel, due to the heat treatment and work it receives in rolling.

> The chemistry, as given, is so locked up with the history of the steel and its treatment, both thermal and mechanical, that in the finished product, although there is an apparently definite chemical composition and as definite physical properties, passing from one heat of steel to another it appears to be unsafe, except as a rough approximation, to use such a formula.

All of these matters are well recognized and I agree with everything except the conclusions, although I have never advocated abandoning the tension and bending tests of small rods rolled from test ingots, as when both methods are used one is a check on the other and enables any trouble that is met to be located more easily than when either system is used alone. This notwithstanding the fact that a number of our steel works only use the chemical composition of the steel on all orders. Some claim that they would not have time to make the number of preliminary tension tests required; other works claim that they have saved $50,000 a year by abandoning their physical tests.

The rejections of rolled structural steels today are much less with the use of the present methods of grading than when the physical tests were relied on alone, and we can now look forward to much greater improvements in grading, if some of the methods suggested by Doctor Howe and Colonel Barba are adopted in the manufacture of structural steels. When this is done even Doctor Burgess will admit that his so-called "rough approximations" have become things of the past.

Doctor Burgess makes it clear in the following, why he considers it would be unsatisfactory to consider manganese content alone: "It would be unsatisfactory to consider manganese content alone; in view of the fact that manganese and sulfur are, within certain limits, always associated, we should preferably speak of the manganese-sulfur ratio. In other words a lower manganese content might be associated with low sulfur than with high sulfur."

Mr. Priestley[12] has gone thoroughly into the troubles caused by manganese-sulfide and their elimination.

Mr. Carney has referred to an old question in the grading of steel by its chemical composition and not considering the effect of manganese on the elastic limit or tensile strength. This was no doubt one of his troubles in keeping the tensile strength within the limits of 8000 lb. allowed, while other steel works who allowed for the effect of manganese had little trouble in working within these limits. In making the very low manganese steel, Mr. Carney overcame the difficulty by reducing the manganese as low as 0.20 per cent., thus getting practically a constant effect for manganese. By using special precautions, he no doubt produced a good clean steel that would flange well, but with a lower elastic limit than steels of the same tensile strength where a higher manganese was used. Some works making this low-manganese steel had difficulty in meeting the high elastic limits called for in our standard specifications, where the dividers were used in checking the elastic limit.

The low manganese referred to in the flange steel in this paper, was caused by unusual loss of manganese in the open-hearth furnace. Steels on the same order that had from 0.35 to 0.45 per cent. manganese would, in some cases, drop to 0.25 or even as low as 0.20 per cent. This was not a clean steel and gave much trouble in flanging. In order to overcome this, the A. S. T. M. embodied the following limits in its specifications for boiler materials and has largely overcome the troubles referred to.

A. S. T. M. Manganese Limits for Locomotive Boiler Plates and Boiler Rivets

	Manganese, Per Cent.
Flange plates ¾ in. or under in thickness	0.30 to 0.60
Flange plates over ¾ in. in thickness	0.30 to 0.60
Firebox plates ¾ in. or under in thickness	0.30 to 0.50
Firebox plates over ¾ in. in thickness	0.30 to 0.60
Boiler rivets	0.30 to 0.50

The following abstracts from the paper of Doctor Howe and Colonel Barba bear directly on this subject:

Loss of Manganese on Addition of Ferromanganese.—(*a*) A further and extremely important indication that the metal has been thoroughly deoxidized before the ferromanganese is added is given by the loss of manganese in this reaction, which should not greatly exceed 10 per cent. of the added manganese. At some well-conducted works, after adding 0.73 per cent. of manganese to a bath containing 0.10 per cent. there is found in the ingots about 0.65 per cent., representing a loss of 0.18 per 100 of steel, or 4.61 per 100 manganese.

(*b*) Such inferences from the loss of manganese can be trustworthy only when the conditions in general, and in particular the time between adding the ferromanganese and determining the residual manganese, are strictly constant.

(*c*) If a larger proportion of the added manganese is lost, taking into account the length of time between adding ferromanganese and teeming. it is good evidence

[12] See page 319.

that the ferrous oxide had not been thoroughly removed from the steel; it is recommended that this point be watched with great care.

Colonel Barba further referred to dirty steel in his discussion of this paper[13] as follows:

In a discussion of this kind we must take into consideration the kind of steel being made and the plant making it. There are places where highly refined killed steel is made. Dirt is a comprehensive term; it can be chemical dirt or it can be mechanical dirt. It is impossible to say that a steel is dirty; that is a purely comparative term. It is necessary to define closely whether mechanical or chemical dirt is meant before it is possible to decide whether a steel is comparatively clean or comparatively dirty. Again, the use to which steel is to be put determines the amount of cleanness that is required.

Sufficient data has been given to explain fully the differences between the low-manganese steel to which I referred and that to which Mr. Carney called our attention. Some steel men have for this steel very unique and suggestive names that places the cause of such trouble where it belongs. Undoubtedly the Pennsylvania Steel Co. secured remarkably good results in grading its steel by results of its physical tests made on small bars as stated by Mr. Carney. The results of grading the steel by its chemical composition were also remarkable, as shown by the following abstract from H. H. Campbell.[14]

NOTE.—Several years have elapsed since the foregoing formulas were deduced. During that time every open-hearth heat made at Steelton has been calculated according to formula and almost every one, acid and basic, has come out within 2500 lb. of the actual strength as determined by the breaking test, except the steels containing manganese in excess of 0.60 per cent. Usually the calculated strength is within 1000 or 1500 lb. of the actual. Our experience proves that the formula represents something and it is used as a check and as a guide in the practical and commercial disposition of hundreds of thousands of tons of steel.

The remarkable results referred to by Mr. Carney and Mr. Campbell were undoubtedly due in part to their use of both methods in grading their steel, as each was a check on the other.

We all feel the same as Mr. Sweetser regarding the need of more information on the troubles caused by irregular working of the blast furnace, scaffolds and slides, etc., giving a resulting pig iron that is unsatisfactory to the foundry men and steel manufacturers. This trouble is being overcome to a great extent by enlarging the hearth and making the walls of the bosh steeper, but as yet we have no satisfactory information on just what oxides of iron cause the trouble. It is to be hoped that the Bureau of Standards will soon be able to assist in solving this problem.

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[13] See page 244.

[14] Manufacture and Properties of Iron and Steel, Ed. 2, 528. New York, 1903. Eng. & Min. Jnl.

The information that Mr. Leibig desires on the physical properties of the steel, to which he refers, can no doubt be acquired by using the A. S. T. M. specifications for automobile steels, which provide for such tests as follows: "It is recommended that tension and bend tests shall be specified for the material as shipped, whenever it is practicable to do so. When physical requirements are specified, requirements as to carbon shall be omitted."

The heat treatment of automobile steels naturally modify some of the disturbing factors referred to in this paper and by Mr. Morris in his discussion. This is well shown by the very uniform results of the physical tests given by Mr. Nelson from their heat-treated crankshafts. These excellent results, as he states, were obtained by taking each heat of steel as a unit and giving it the heat treatment that its chemical composition indicated was required.

Correspondingly uniform results between chemical composition and physical properties in heat-treated automobile steels will no doubt be shown in the charts referred to by Mr. Morris. This is the most important work that has been undertaken, as the results will be based on the every-day practice of steel works in grading the steel, followed with the every-day heat treatments that have been found to give the most uniform results. Thus practically doing this month from start to finish what was found satisfactory in former work. When trouble occurs the question of the relation between the chemical composition and the physical properties of the steel is not questioned but errors in the chemical analyses and heat treatment are sought in the effort to locate the trouble.

Mr. Morris is undoubtedly aware that each mill takes into account the treatment its steel receives in rolling, and makes allowances for this in deciding the chemical composition to be used for a desired tensile strength. In doing this the mills do not require any formula, as they have tabulated records of what is required, based on their every-day practice for any standard orders of structural steels. No doubt the plants at Steelton and Bethlehem, by the use of such charts, are getting equally satisfactory results in meeting the requirements of the specifications in their finished products.

The specifications of the A. S. T. M. provide for standard methods of testing and standard methods of analysis and now a committee is working on standard methods of taking drillings for chemical analysis, covering the location and depth of hole, etc., in order to secure representative samples. This covers some of the points referred to by Mr. Morris.

Troubles from improperly prepared test pieces is much greater in the high-carbon steels than in the ordinary structural steels, and in some cases it is necessary to polish the test pieces to remove tool marks or scratches before satisfactory results can be obtained. The best evidence of troubles caused by these sources is often found in broken parts from

automobiles, where such pieces have been broken by ordinary use from a fracture that started from small tool marks, which would often be overlooked by those accustomed to working in lower carbon steels.

The next step is to have the steel manufacturers' grading of structural steels in every-day practice comply with the chemical and physical

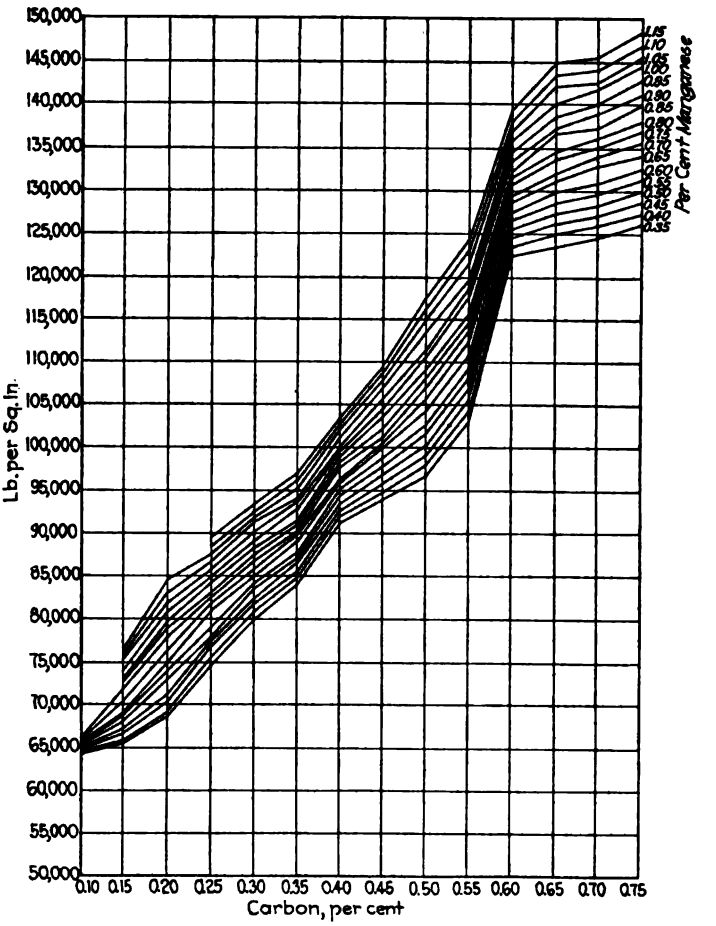


FIG. 1.—AVERAGE RESULTS OF TESTS ON ¾-IN. ROUND BARS ROLLED FROM TEST INGOTS OF BASIC OPEN-HEARTH STEEL WITH PHOSPHORUS UNDER 0.031 PER CENT.

requirements of the A. S. T. M. specifications for basic open-hearth structural steels. The object is to get as far away as possible from any formula, by the use of the mills working tables that merely give what their practice has shown to be required to produce the best results in rolling.

It would only require three tables to classify this working data for structural steels (plates, shapes and bars), each subdivided for light, medium and heavy material, according to practice. A fourth table for rivet rods could be added to advantage. These tables could be somewhat as shown, the various data for the thicknesses being arranged in

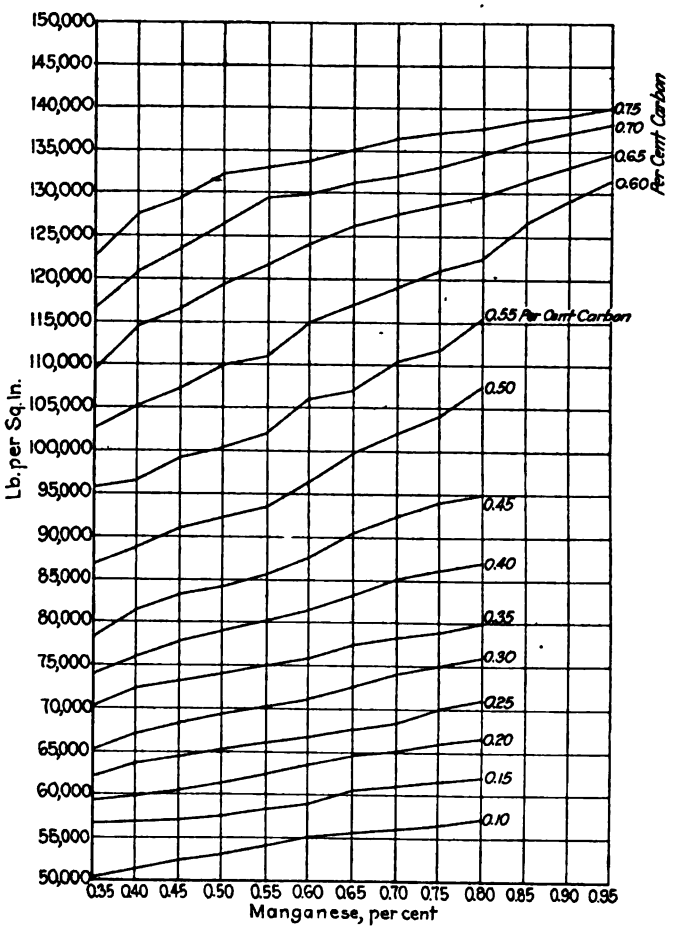


FIG. 2.—RESULTS OF CARBON VARIATIONS IN STEEL SHOWN IN FIG. 1.

groups. This would bring up to date the advances that have been made in the grading of structural steels during the past thirty years; it would take account of our present methods and working conditions, it would also give data for further improvement as suggested.

I am very much obliged to Mr. Waterhouse for offering the data used at the works with which he is connected, and I trust that other works

will do the same in order that a full set of these tables can be presented at our next annual meeting for consideration and discussion.

The diagrams shown in Figs. 1 to 4 are based on the actual figures from the large working tables of steel works A for basic open-hearth steel and bessemer steel, and have nothing whatever to do with any

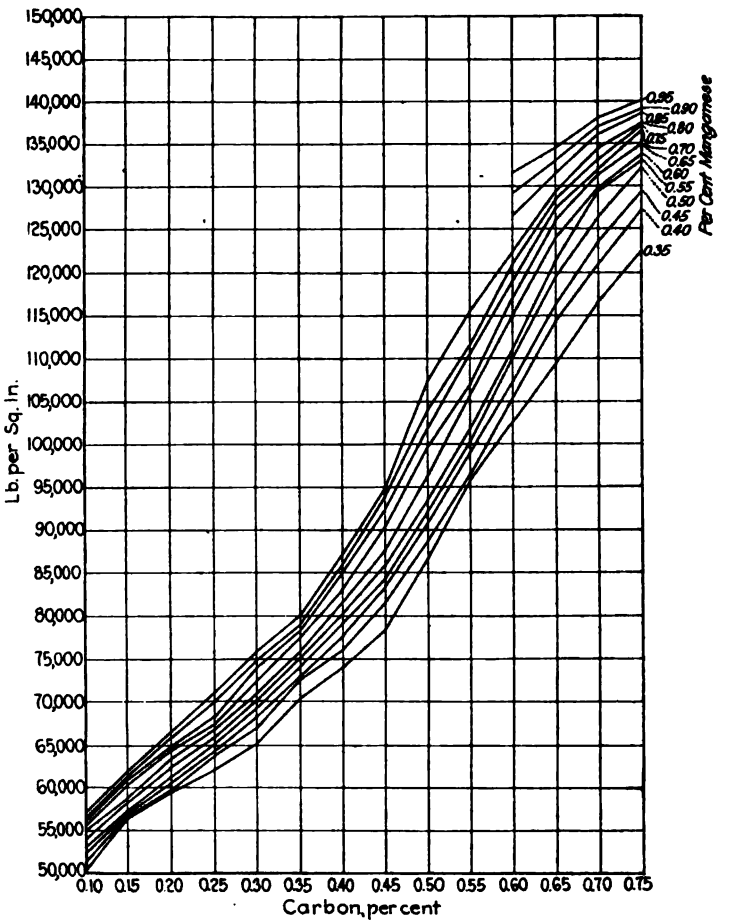


FIG. 3.—AVERAGE RESULTS OF TESTS ON ¾-IN. ROUND BARS ROLLED FROM TEST INGOTS OF ACID BESSEMER STEEL.

formula. For open-hearth basic steel, Figs. 1 and 2, the manganese lines are plotted for every 0.05 per cent. from 0.35 to 0.95 per cent. and the carbon lines for each 0.05 per cent. from 0.10 to 0.75 per cent. For bessemer steel, Figs. 3 and 4, the manganese lines are plotted for every 0.05 per cent. from 0.35 to 1.15 per cent. and the carbon limits for each 0.05 per cent. from 0.10 to 0.75 per cent. Both the carbon lines and the

manganese lines are comparatively similar in the basic open-hearth steel. In the bessemer steel, the large break in the carbon lines from 0.55 to

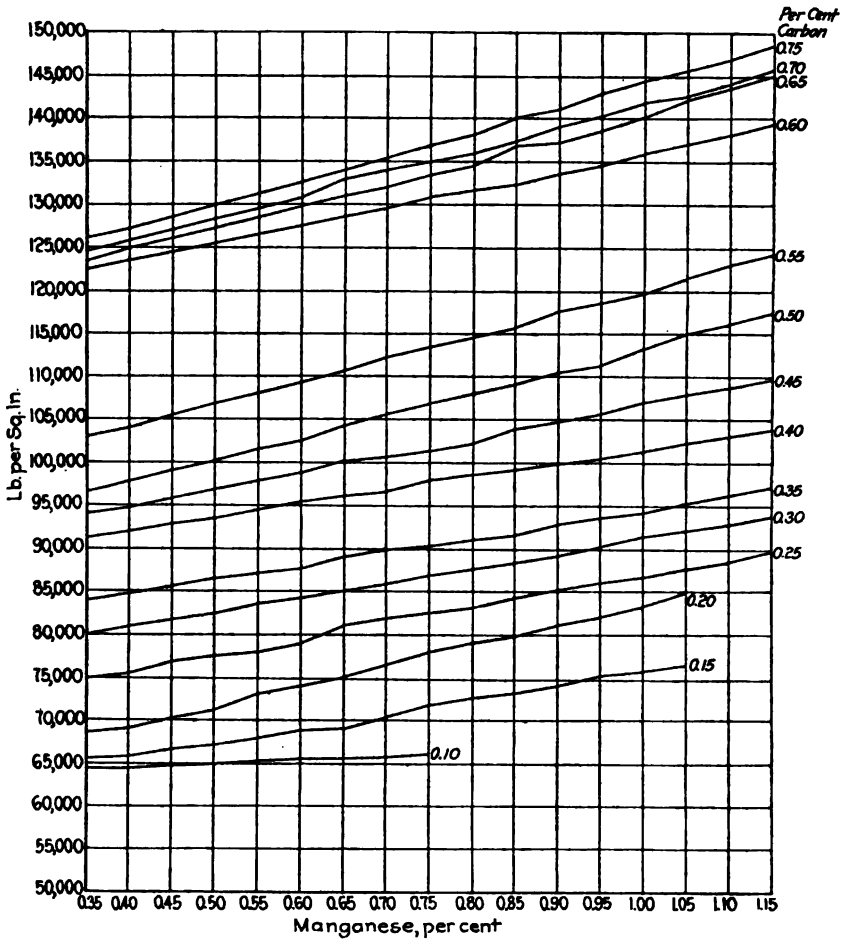


FIG. 4.—RESULTS OF CARBON VARIATIONS IN STEEL SHOWN IN FIG. 3.

0.60 per cent. is caused by a much higher silicon in steels of 0.60 per cent., and over carbon that is used for springs, etc.

Basic Open-hearth Steel Plates, A. S. T. M. Specifications

Class		Firebox		Flange		Bridge		Ship		Cars		Locomotives		Buildings	
Tensile strength, lb. per sq. in.....		52,000–62,000		55,000–65,000		55,000–65,000		58,000–68,000		50,000–65,000		55,000–65,000		55,000–65,000	
Phosphorus, per cent.		Not over 0.035		Not over 0.04		Not over 0.04		Not over 0.04		Not over 0.04		Not over 0.05		Not over 0.06	
Manganese, per cent..		0.3–0.50*		0.30–0.60*											
Steel Works	Thickness, Inches	Carbon	Manganese	Carbon	Manganese	Carbon	Manganese	Carbon	Manganese	Carbon	Manganese	Carbon	Manganese	Carbon	Manganese

* NOTE.—Firebox plates ⅝ in. or under in thickness, manganese, 0.30 to 0.50 per cent.
Firebox plates over ⅝ in. in thickness, manganese, 0.30 to 0.60 per cent.
Flange plates, all thicknesses, manganese, 0.30 to 0.60 per cent.
Where phosphorus is over 0.04 per cent., give reduction in amount of carbon used for each 0.01 per cent. phosphorus.

Nitrogen in Steel and the Erosion of Guns*

By H. E. Wheeler, Chicago, Ill.

(Lake Superior Meeting, August, 1920)

The work described was carried out during 1917 and 1918 at the testing laboratory of Watertown Arsenal at the instigation of the Nitrate Division and later with the concurrence of the Cannon Section of the Ordnance Department, U. S. A. The experiments follow three principal lines of work: First, the effect of nitrogen under pressure on steel containers of various compositions at a red heat; second, the effect of decomposing ammonia on various alloy steels, iron, and non-ferrous alloys; third, a new theory of the erosion of guns in respect to the effect of nitrogen in steel.

Part I

In the Haber process for the manufacture of ammonia from its elements, it is necessary to have nitrogen and hydrogen of 1500 lb. per sq. in. (105.5 kg. per sq. cm.) at a temperature of 500 to 600° C. The steel containers for these gases gave trouble by failing without apparent cause.

When the General Chemical Co. began to develop its method for the production of ammonia, it experienced the same difficulty and, knowing that the Haber process had solved the difficulty by the use of alloy steels, it made several small steel bottles of different compositions and kept them filled with these gases at this pressure and temperature until they failed. The time of service varied from a few days, for the plain steel casting, to two years for a chrome-vanadium forging. Four of these steel bottles were sent to this laboratory for investigation; they were a plain carbon-steel forging, a nickel-steel forging, a chrome-vanadium steel forging, and a chrome-steel forging. The time of service was as follows: plain carbon steel, 4 mo.; nickel steel, 6 mo.; chrome-vanadium steel, over 2 yr.; chrome steel, 4 mo. When these containers were cut open and the cross-section surface polished, they showed an inside zone with a different luster from the rest of the metal. Upon etching, this zone was almost unaffected while the rest of the steel etched normally.

* Published by permission of the Ordnance Department, U. S. A.; the Department is not to be considered as officially concerned with the contents.

Complete chemical analysis is given in a section devoted to analytical results. The carbon content inside to outside varied as follows:

	Per Cent. Carbon Outside	Inside
Plain carbon steel	0.35	0.05
Nickel steel	0.43	0.41
Chrome-vanadium steel	0.54	0.29
Chrome steel	1.06	0.58

The structureless zone remains unaffected when etched with sodium picrate, and is not affected by quenching; see Figs. 1 to 6. The penetration was of sufficient depth to make it possible to cut a piece out of the affected area large enough to forge lightly in the cold. With very little cold working, the hardness increased rapidly. The hardness by scleroscope was 20 to 25 before working, and 75 after working.

Fig. 1.—Nickel-steel container split lengthwise, showing zone that remains bright after etching 15 sec. with 4 per cent. nitric acid.

Fig. 2.—Cross-section of chrome-steel container showing zone of penetration and cracks after etching 15 sec. with 4 per cent. nitric acid. × 2. Distortion due to camera.

Much more recently a pipe used to transmit these hot gases under similar pressure failed in service and was sent in for investigation. It was 0.13 per cent. carbon steel; its structure is shown in Figs. 7 and 8. This effect was at once proclaimed decarburization. From the German patent literature, it would appear that this explanation has been used

from the first. However, both the nickel steel and the chrome steel were far from decarburized by analysis, and yet had the same appearance as the carbon steel. At the suggestion of the Nitrate Division, under

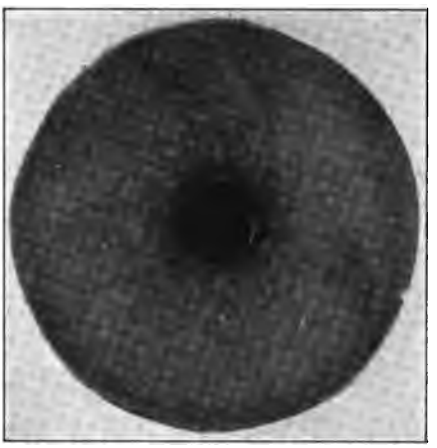


FIG. 3.—CHROME-VANADIUM STEEL CONTAINER CROSS-SECTION, SAME LIGHTING AS IN FIG. 2, AFTER ETCHING 15 SEC. WITH 4 PER CENT. NITRIC ACID. × 2. NO APPRECIABLE EFFECT.

FIG. 4.—CHROME-STEEL CONTAINER AFTER HEATING TO 1000° C., AFTER ETCHING 15 SEC. WITH 4 PER CENT. NITRIC ACID. × 50. CROSS-SECTION AT JUNCTION OF ZONES.

whose direction this work was carried out, the cylinders were analyzed inside and outside for nitrogen. However, they showed no unusual

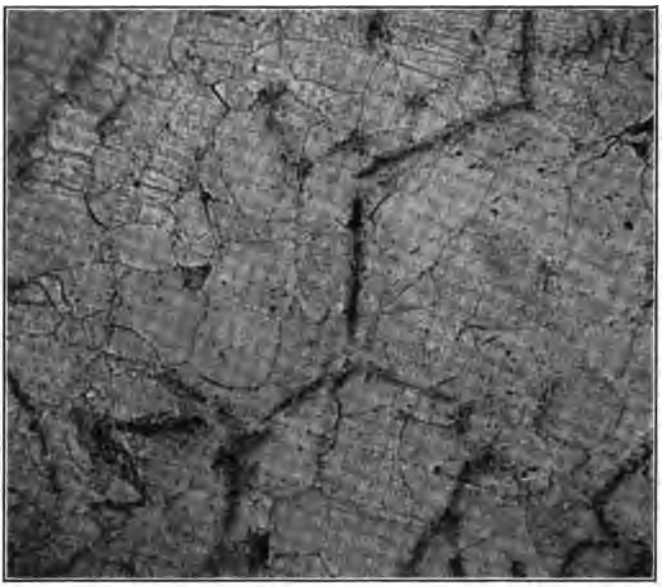


FIG. 5.—SAME AS FIG. 4, WITHIN ZONE OF PENETRATION, AFTER 15 SEC. WITH 4 PER CENT. NITRIC ACID. × 500. BLACK LINES ARE SMALL CRACKS.

FIG. 6.—SAME AS FIG. 4, IN ZONE OF UNAFFECTED METAL, AFTER ETCHING 15 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

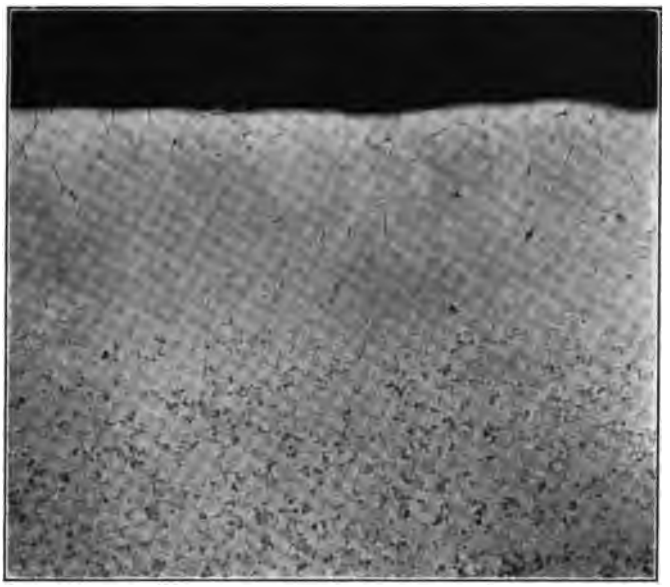


FIG. 7.—CROSS-SECTION OF 2-IN. PIPE INSIDE EDGE OPPOSITE POINT OF FAILURE, SHOWING ZONE OF PENETRATION. ETCHED 20 SEC. WITH PICRIC ACID. × 50.

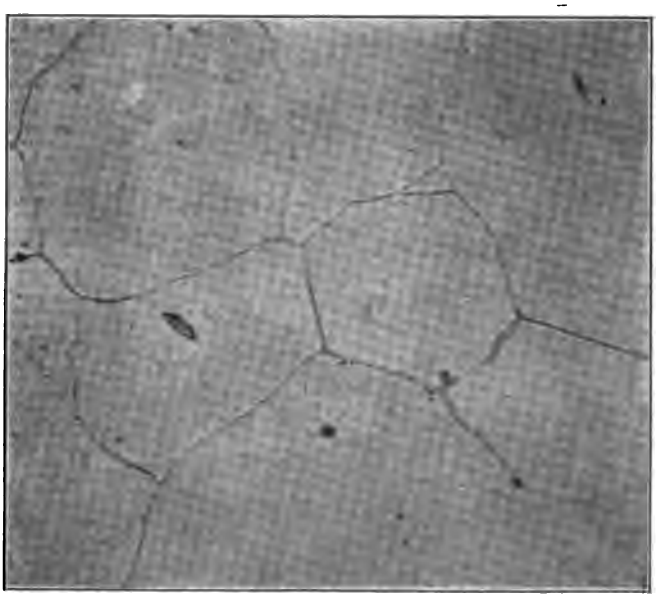


FIG. 8.—SAME AS FIG. 7, WITHIN ZONE OF PENETRATION. ETCHED 20 SEC. WITH PICRIC ACID. × 500.

amount of nitrogen, and the nitrogen content hardly varied appreciably from inside to outside. This is easy to understand now since it is doubtful whether the methods employed gave all the nitrogen.

Vacuum Experiments

An investigation going on at this laboratory at this time on the occluded gases in steel, in charge of Lieut. E. H. Hemingway, gave one more possibility, so a sample of one of the containers was treated in the apparatus with which he was working. With this apparatus it is possible to hold a piece of steel for several hours at 1000° C. under a very high vacuum, and to collect and analyze the resultant gases. The results were not conclusive, as far as gas analysis was concerned; but in repolishing the sample it was found that the cracks had closed up and that there was considerably more pearlite in evidence than before, as will be seen by the following photomicrographs.

To prove that the heat alone without vacuum did not produce this result, the chrome container was normalized at 1000° C. and showed no change, other than a slight penetration of the white zone into the normal metal and the closing of the cracks. This is not merely a surface reaction, because when the pieces were cut in two they showed the same effect throughout. Apparently the pearlite was held in solution by some gas, probably nitrogen, which was removed by prolonged heating in vacuum. Similarly, in case of the pipe referred to above, a vacuum treatment restored the pearlite as shown in Fig. 12.

It was thought possible that the cracks might be due to the difference in the specific gravity of the steel, and this therefore was very accurately determined inside and outside in a Richard's pycnometer under toluene. The results are as follows: outside, unaffected metal, 7.743; inside, affected metal, 7.682. This difference is so slight that it seems more likely that the disappearance of the cracks was due to relieving of stresses that had been set up by the pressure. These results are only approximate on an absolute basis, but are relatively correct to the third decimal place.

Andrews'[1] work showed that steel melted under a pressure of nitrogen took up some of the nitrogen and gave it up only very slowly with heat and vacuum; he concluded that several weeks of such treatment would be necessary to remove all the nitrogen. His cooling curve showed that a 0.16 per cent. carbon steel would absorb enough nitrogen, when melted quickly under pressure of the gas, to suppress completely its three critical points. When the steel is then heated in vacuum for varying lengths of time and cooling curves taken between each treatment, these points reappear in a way that gives some inkling of the combina-

[1] J. H. Andrews: *Jnl.* Iron and Steel Inst. (1912) **86**, 210.

FIG. 9.

FIG. 10.

FIG. 9.—CROSS-SECTION OF NICKEL-STEEL CONTAINER, THREE ADJOINING PHOTOMICROGRAPHS BEFORE VACUUM. ETCHED 20 SEC. WITH PICRIC ACID. × 50.

FIG. 10.—SAME AREA AS FIG. 9 AFTER HEATING IN VACUUM TO 1000° C. SEVERAL HOURS. CRACKS CLOSED, ZONE OF PENETRATION NARROWED. ETCHED 20 SEC. WITH PICRIC ACID. × 50.

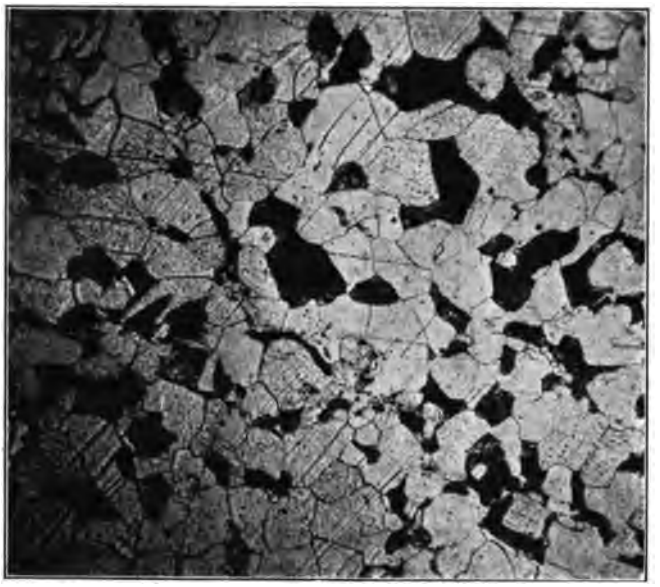


FIG. 11.—SAME AREA AS FIG. 5 AFTER VACUUM TREATMENT. ETCHED 20 SEC. WITH PICRIC ACID. × 500.

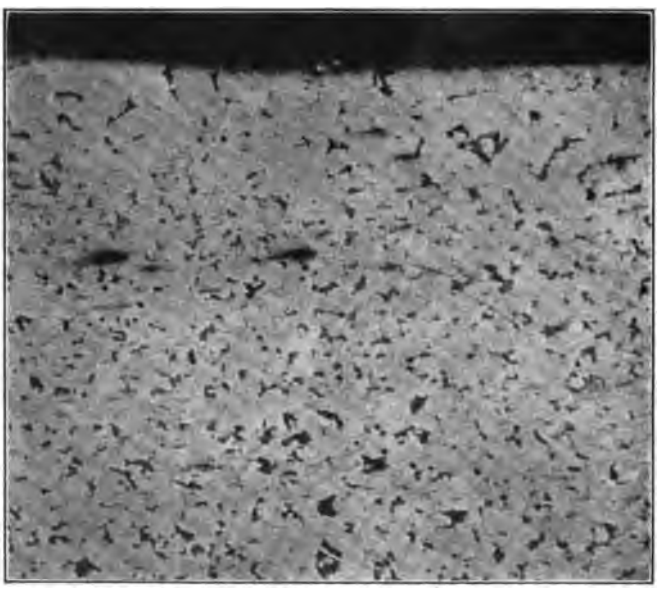


FIG. 12.—SAME AREA AS FIG. 7 AFTER VACUUM TREATMENT. ETCHED 20 SEC. WITH PICRIC ACID. × 50.

tion that takes place. The upper two points become gradually sharper as the nitrogen is removed, but are neither raised nor lowered. The Ar_1 point first becomes evident at a temperature well below that at which it formerly occurred, but still considerably above room temperature. As more nitrogen is removed the point becomes sharper and is raised until it finally reaches its usual position and intensity. From Andrews' work then, evidently, nitrogen can dissolve in molten steel under pressure and affects the crystallization of the carbide. These cylinders seem to indicate that nitrogen can also dissolve in solid steel with heat and pressure, giving an effect similar to that produced by adding more nickel or manganese. There is no evidence in all the literature, nor in this work, that molecular nitrogen will react with iron in the absence of carbon under any conditions.

Part II

A few preliminary experiments on alloy steels indicated that a stream of ammonia passed over them for a long period of time, at about 650° C., gave an effect very similar to that observed in the cylinders described in Part I. High-pressure experiments with molecular nitrogen are difficult, dangerous, and take a great deal of time, so it was thought that a study of the effect of nascent nitrogen on various steels might throw some light on their general behavior and be a good method of elimination. The furnace used consisted of an inside glazed fused silica tube, electrically heated, and arranged so that the sample of steel being treated could be moved from the hot to the cool parts of the furnace without opening it to the air, as described by Tschischewski.[2] In each case a small cylinder of metal about 5/8 in. (15.6 mm.) in diameter was used as a sample, and before treating in ammonia it was cut across one end with a saw in the direction of the axis to a depth of 1/8 in. The piece was put in the furnace and brought up to the temperature of the experiment (usually 650° C.), then the ammonia was turned on from a tank of the compressed gas, and the flow adjusted so that when the outcoming gases were passed through ammonium hydroxide and then through sulfuric acid they appeared to be 50 per cent. decomposed. This was continued for 20 hr., the temperature being held quite constant; at the end of that time the specimen was moved to a cooler part of the furnace. When this piece was cut clear through on a plane perpendicular to the original saw cut and polished and etched, the effect of the penetration could be very easily observed.

Carbon Series

Norway Iron.—Much work has been done on the effect of decomposing ammonia on low-carbon irons but most of the investigators have ignored

[2] N. Tschischewski: *Jnl.* Iron and Steel Inst. (1915) **92**, 47.

FIG. 13.—NORWAY IRON TREATED IN NH_3 20 HR. AT 750° C. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500. FIVE ADJOINING EXPOSURES FROM EDGE, SHOWING CARBURIZED EDGE AND NEEDLES.

the effect of carbon impurities in the ammonia. This was first pointed out in *Stahl und Eisen*.[3] The writer believes that undue stress has been laid on iron nitride in respect to the effect of nitrogen in iron and steel. Nascent nitrogen from the decomposition of ammonia will react with pure iron to form iron nitride, Fe_2N; this compound is only stable up to 450° C. and is entirely decomposed well below the melting point of steel. It decomposes in dilute acids to form the ammonia salt quantitatively; this is the basis of most methods of analysis for nitrogen in steel. Another method, which has the advantage of less contamination by the reagents, is to pass hydrogen gas over the nitride at 425° C. and to wash out the resultant ammonia in a standard acid, using methyl red as an indicator. Either method gives the nitride nitrogen only.

A sample of iron was heated in purified dry hydrogen to constant weight and then in dry ammonia until there was no further gain in weight at 425° C.; the gain corresponded to the formula Fe_2N. There was no gain in carbon by the iron at this temperature, the content being 0.06 per cent. before and after treatment. This sample was then heated in purified dry hydrogen gas at 425° C. to constant weight, and the resultant ammonia washed out in standard acid and the excess acid titrated, using methyl red. The loss in weight and the titration both checked to the formula Fe_2N very closely, the variation being only a few hundredths per cent.

Iron nitride is no more metallic than iron oxide, and the writer seriously questions its ever having been found as a metallographic constituent of steel. The effect of ammonia on very low-carbon iron is illustrated in the German work referred to above, and also in Fig. 13. This is a composite picture made up of five adjoining exposures, at 500 diameters, of a piece of Norway iron of 0.06 per cent. carbon treated for several hours in ammonia; it also shows the carburized edge noted by these investigators. Since careful samp-

[3] (Dec., 1914) 1817 (abstract in *Iron Age*, Feb. 17, 1916).

ling shows that the inside of this piece has not lost carbon, the edge must have been carburized by pyridine impurities in the ammonia. The Widmannstättian bands will be referred to later. This zone is by analysis from 0.40 to 0.90 carbon.

Some ammonia manufactured by the catalytic process at the U. S. Nitrate Plant No. 1, at Sheffield, was obtained and Norway iron treated in this gas showed somewhat less gain in carbon. In 48 hr. at 750° C., one piece gained enough carbon so that filings from the edge analyzed

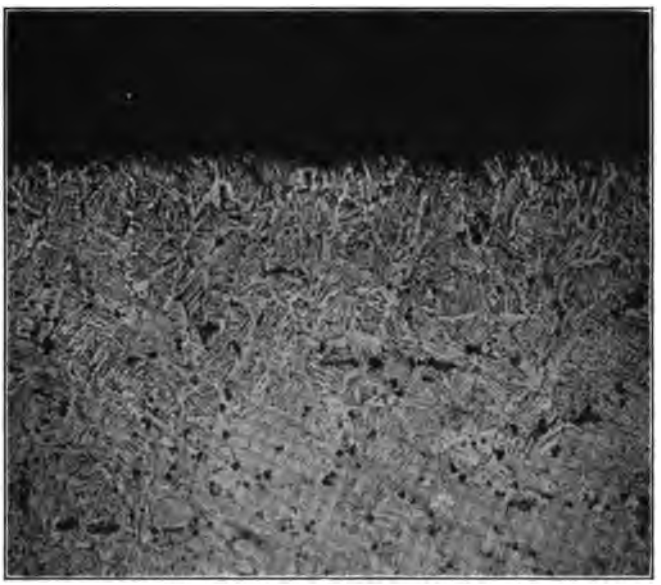


FIG. 14.—ANOTHER VIEW OF CARBURIZED EDGE OF FIG. 13, SHOWING WIDMANNSTÄTTIAN STRUCTURE. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 50.

0.64 per cent. C. The carbon in this case is evidently not pyridene, but residual carbon monoxide, dioxide, acetylene, or methane, which escaped the purification process. Figs. 14 to 17 show these structures in more detail. The fine lines, needles, slip bands or Neuman bands, are plainly evident. They are not made any more numerous by straining the piece, as would be expected if they were slip bands caused by the extreme brittleness of the nitrogenized ferrite. Strain followed by annealing does not increase the number of these lines, as would be expected were they due to twinning. They seem to be associated with some critical carbon content. To call them iron nitride is a long unwarranted step in the dark.

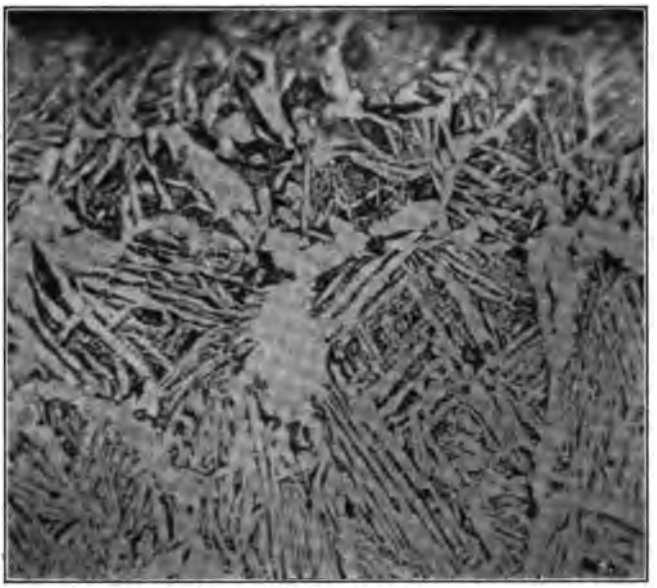


FIG. 15.—SAME AS FIG. 14. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

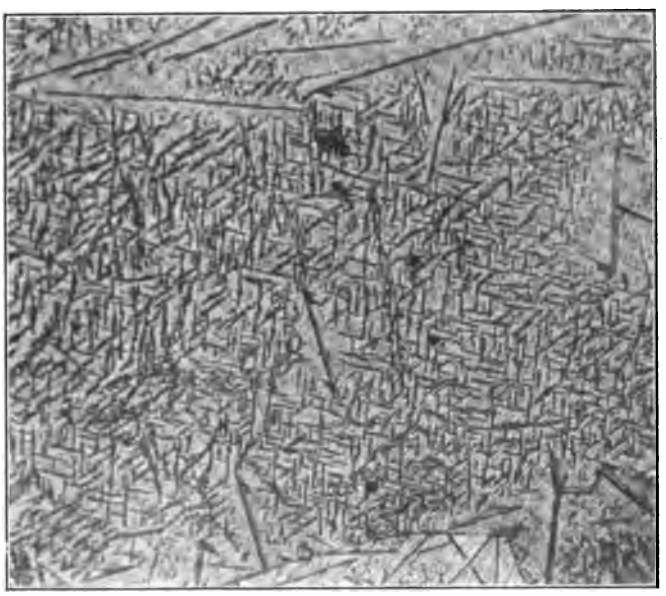


FIG. 16.—NORWAY IRON TREATED 20 HR. AT 650° C. IN SYNTHETIC AMMONIA, SHOWING TYPICAL SMALL NEEDLES. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

FIG. 17.—SAME AS FIG. 16, SHOWING TYPICAL LARGE NEEDLES. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

FIG. 18.—WASHED METAL, TREATED IN NH_3 FOR 20 HR. AT 650° C.; NO EFFECT ON EDGE. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

White Cast Iron and Washed Metal.—The difference in behavior of washed metal and white cast iron is remarkable and, so far, inexplicable. When washed metal of about 3.50 per cent. combined carbon is treated in ammonia at 650° C., it is hardly affected. At 750° C., there is only a slight decarburization; the metal is extremely resistant. See Figs. 18 and 19.

White cast iron of about the same content of combined carbon might be expected to act in the same way. The metal is not penetrated at all, as far as can be seen, but the surface becomes coated to a depth of from $\frac{1}{16}$ (1.5 mm.) to $\frac{1}{8}$ in. with iron nitride. This can be scraped off easily

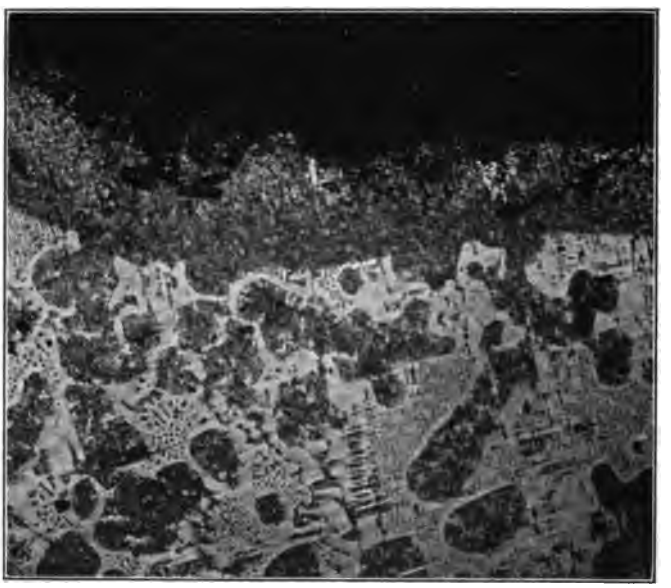


FIG. 19.—WASHED METAL TREATED IN NH_3 20 HR. AT 750° C.; EDGE DECARBURIZED TO FORM PEARLITE. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 50.

with a penknife and analyzed, and shows that the carbon content has been reduced to 1 per cent., the remainder being Fe_2N, by analysis. This experiment was repeated several times. Always the white cast iron came out of the furnace with a heavy lead-colored coat of iron nitride, while the washed metal came out bright. Too much emphasis cannot be laid upon this fact, since it was the only case in this research where there was a noticeable formation of iron nitride on a solid piece. Pulverant iron by hydrogen could be quantitatively converted to the nitride, but on solid pieces there was not another single case where there was even the slightest evidence of nitride. The analysis throws no light on the peculiar behavior of white cast iron unless the effect can be attributed to the sulfur or phosphorus.

	Carbon	Manganese	Silicon	Sulfur	Phosphorus
White cast iron.....	2.15	0.12	0.33	0.208	0.20
Washed metal.....	3.65	None	None	0.02	0.01

Between these two extremes of carbon content, the medium-carbon steels are affected by the formation of a structureless zone, as in the case of the cylinders in Part I. At 650° C. the ferrite seems to offer almost no resistance to the penetration of nascent nitrogen; the pearlite and cementite do. The cementite is first reduced to pearlite evidently by losing carbon. Pearlite disappears as the penetration proceeds, but experiments show that the carbon is still present but in solution; therefore, the higher the carbon content the slower is the penetration. To demonstrate this point by photomicrographs would take considerable space so the statement is left unsupported by proof for the sake of brevity, but the work in nickel steels will throw further light on it.

Analysis.—No one knows what nitrogen content in steel is detrimental or in what form it exists, so it would seem reasonable to suppose that this knowledge must come before a method of analysis can be devised. Andrews has offered the suggestion that alloys which are entirely soluble in ferrite in the solid and liquid state and do not form compounds with it nor with carbon are effective in lowering the Ar_1 point in proportion to their atomic volume. Doctor Langenberg has suggested to the writer that the work of Prof. T. W. Richards[4] on the compressible atom might be successfully applied to this problem. Professor Richards showed good evidence that the space occupied by any substance as a gas at the critical point is completely filled with the atoms comprising it and that though this volume is greatly affected by affinity, cohesion, etc., it is more or less characteristic of any element in any of its combinations. On this basis, it is evident that a few hundredths of 1 per cent. nitrogen would be as effective in steel as several per cent. of nickel, for instance; results seem to bear out this conclusion.

Surely any method for determining nitrogen in steel which depends on the conversion to NH_3 is open to the objection that dissolved nitrogen may not be reduced. In the case of the cylinders in Part I and many of the pieces treated in ammonia, the amount of nitrogen that could be converted to NH_3 was apparently irrespective of the effect noticeable in the microstructure.

When sections of the affected zones of the cylinders were cut out and dissolved in the double chloride of copper and potassium, the gases evolved showed no remarkable nor consistent results in respect to nitrogen, though the temperature was very carefully regulated. Fine filings of this affected steel heated in molten sodium or sodium carbonate gave no trace of cyanide. When dissolved in H_2SO_4, no cyanide is evolved.

[4] T. W. Richards: *Jnl.* Amer. Chem. Soc. (Dec., 1914) **36**, 2417.

The vacuum method seems promising but the technique is difficult. Although the apparatus at Watertown is entirely of glass and fused silica, it did not include a direct method for nitrogen and so was decidedly unsatisfactory on such small amounts.

Some pieces previously treated in ammonia gave off large volumes of gas under vacuum, which analyzed sometimes as high as 80 per cent. nitrogen. Again the quantity would be small and the nitrogen as low as 12 per cent. Lieutenant Hemingway has shown that surface is a large factor in this problem in general.

Pure Metals and Special Alloys.—Henderson[5] found that all pure metals, with the exception of tungsten, were greatly altered by decomposing ammonia; the effect he attributed to the continuous formation and decomposition of nitride. In this work, the writer was first led astray into a study of alloy steels based on the effect of nitrogen on the pure metal used as alloy. But it soon became evident that in steel the alloyed elements did not combine with the nitrogen but affected its penetration only as they affected the carbide, so this line of investigation was dropped. Several special alloys show good resistance to the action of decomposing NH_3. Among those that proved quite resistant were stellite, monel metal, and nichrome.

Alloy Steels.—Before taking up the more complicated subject of alloy steels, it should be pointed out that this method of investigation cannot be applied sweepingly to all kinds of steel without taking carefully into consideration the variables that determine the extent of the effect that is being observed; namely, the depth of the case formed by the nitrogen. First, the ammonia is effective in proportion to the concentration of nascent nitrogen on the surface being studied. This is affected by the rate of flow, the temperature, the hot surfaces previously encountered, and the surface of the piece itself.

Next, on low-carbon samples, the carbon impurities in the ammonia must be reckoned with. These consist of pyridine, carbon monoxide, acetylene, etc., depending on the source of the ammonia. They do not act as carburizers unless the carbon content is fairly low. With very high carbon content the action is reversed, the hydrogen acting as a decarburizer Both reactions seem to require a temperature higher than 425° C. Also, it is necessary, in making comparisons, to consider the state of existence of the carbide during the experiment in reference to its critical points, its previous heat treatment, hot or cold work, etc.

Another variable, quite difficult to control but powerful in its effect, is the rate of cooling the sample through its critical range after the experiment. A factor that enters very little in this work, but is of great im-

[5] G. G. Henderson and G. T. Beilby: *Jnl.* Chem. Soc. (1901) **79**, 1245.
G. G. Henderson and J. C. Galletly: *Jnl.* Soc. Chem. Ind. (Apr. 30, 1908) **27**, 387.

portance in pressure experiments, will be called penetrability. It will be referred to later.

The alloy steels tested are listed only by analysis and in a general way indicate the source. Many were prepared to order by the Bureau of Mines, and those that were needed quickly were made in the laboratory by the thermit process. Although this work covered all practical and many special steels, as shown by the table of analyses, by far the most of the work was centered on nickel steels, since these are largely used in ordnance and the writer early in the work came to the conclusion that he was dealing with an effect similar to erosion. Also, nickel steels can be treated above their critical change at temperatures low enough to be practicable with ammonia.

Nickel Steels.—First sample (Bar No. 4011-8), a 0.35 per cent. C 3.00 per cent. Ni steel with an Ar_1 point at 605° C. and an Ac_1 point

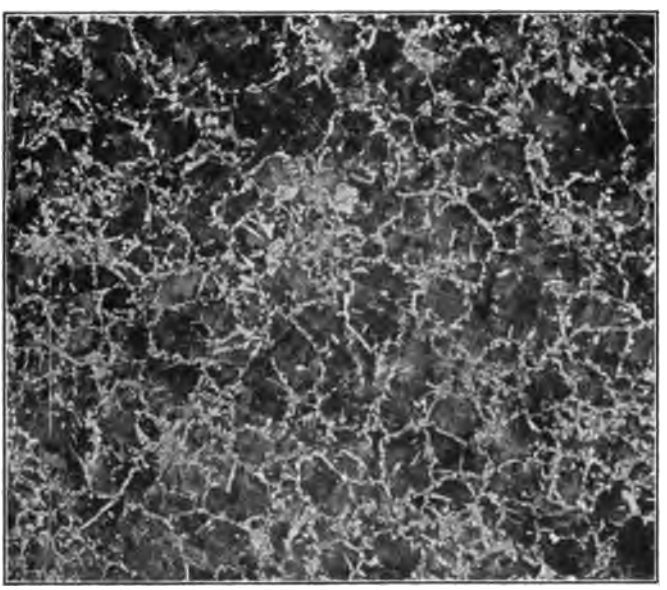


FIG. 20.—BAR NO. 4011-8. NICKEL STEEL 0.35 PER CENT. C., 3.00 PER CENT. NI. TREATED 12 HR. IN NH_3 AT 650° C. ETCHED 15 SEC. WITH 4 PER CENT. NITRIC ACID × 50. BELOW CRITICAL CHANGE; CENTER NOT AFFECTED.

at 705° C. Treated for a few hours in NH_3 at 650° C., it showed a white zone at the surface but the center structure was unchanged as in Fig. 20. Another piece of the same metal was heated first to 850° C., cooled to 650° C., and then treated 12 hr. in ammonia. The edge effect was much deeper and graded off into martensite, as shown in Fig. 21. The center structure was changed, as shown in Fig. 22. Repolishing and etching with a copper-bearing reagent gives the reverse, as shown in Fig. 23.

FIG. 21.—SAME SAMPLE AS IN FIG. 20 TREATED 12 HR. IN NH_3 AT 650° C.; FIRST HEATED TO 850° C. SHOWS MARTENSITE BETWEEN OUTER AND INNER ZONES. × 500.

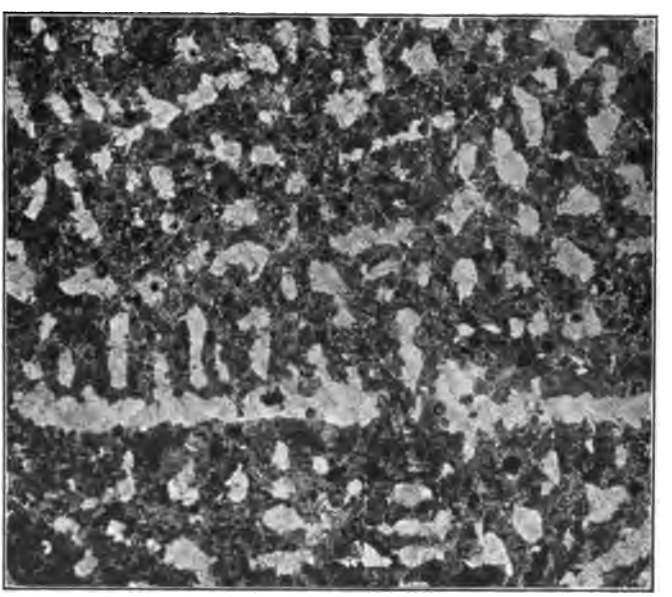


FIG. 22.—SAME AS FIG. 21; INSIDE STRUCTURE. ETCHED 15 SEC. WITH 4 PER CENT. NITRIC ACID. × 50.

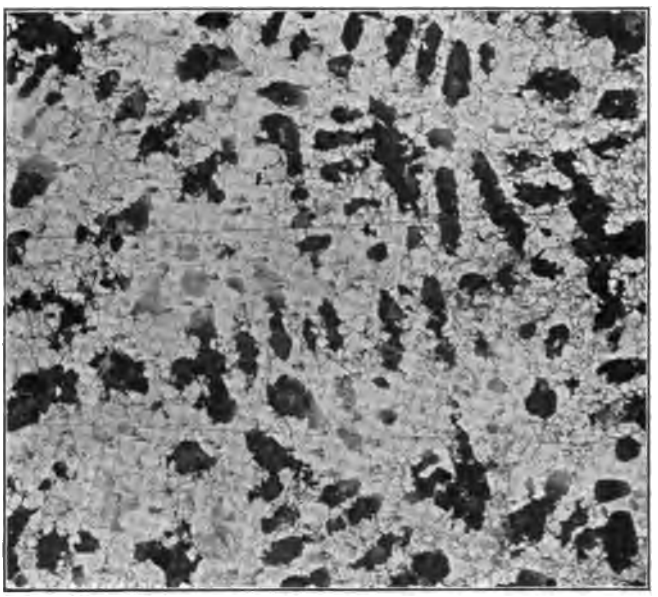


FIG. 23.—SAME AS FIG. 22 REPOLISHED AND ETCHED WITH COPPER-CHLORIDE REAGENT. × 50.

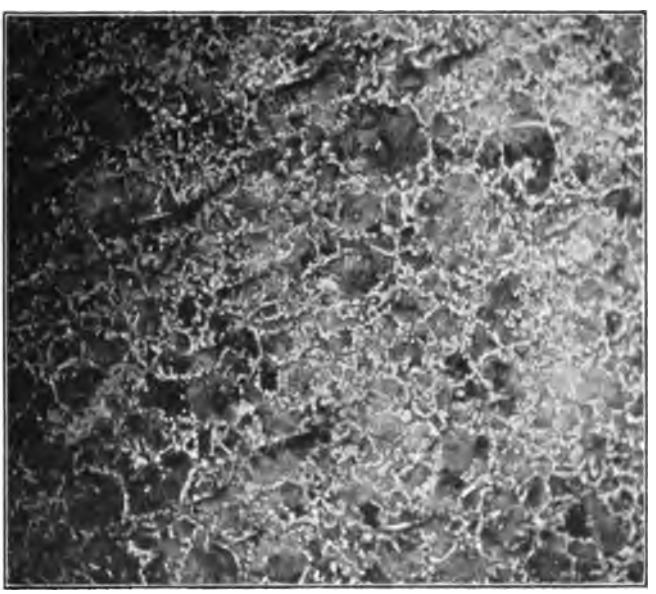


FIG. 24.—SAME AS FIG. 23 AFTER VACUUM TREATMENT. × 50.

This reagent was made up as follows: CH_3OH, 100 c.c.; H_2O, 18 c.c.; Conc. HCl, 2 c.c.; $CuCl_2$, 1 gm.; $MgCl_2$, 4 gm. This sample, when treated several hours in a vacuum at 1000° C., polished and etched again with the copper-bearing reagent, is shown in Fig. 24. This showed that the

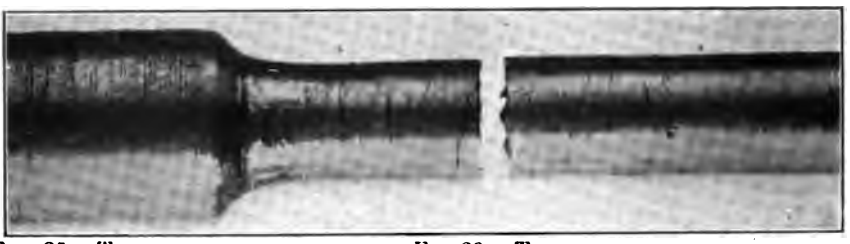


FIG. 25.—TENSILE BAR OF STEEL USED IN FIG. 20. TREATED ABOVE CRITICAL CHANGE IN NH_3 AT 650° C. FOR 15 HR. HARD OUTSIDE LAYER NOT DUCTILE. × 3.

same steel treated at the same temperature (650° C.) was affected only on the surface when in the crystalline state and all through the piece when in the solid-solution state.

A tensile bar turned from this sample and treated in NH_3 15 hr. at

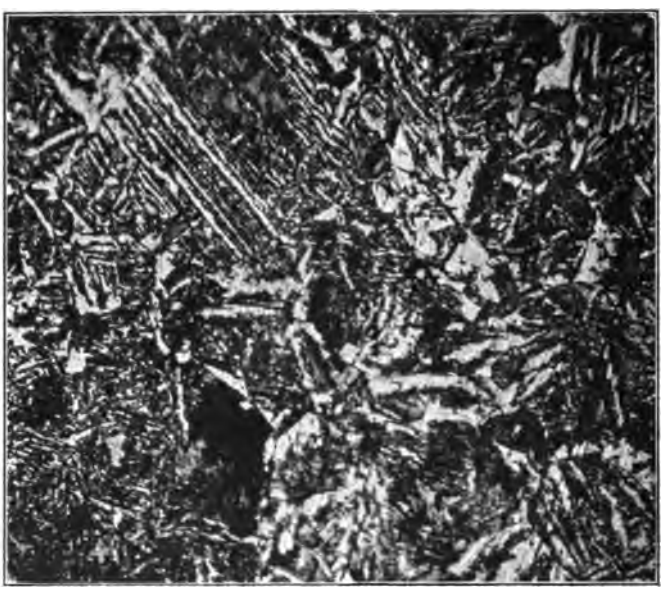


FIG. 26.—CROSS-SECTION OF BAR SHOWN IN FIG. 25. ETCHED 20 SEC. WITH PICRIC ACID. × 500. CENTER STRUCTURE SHOWING SMALL-SCALE WIDMANNSTÄTTIAN.

650° C. (first heated to 850° C.) came out of the furnace so hard on the surface that it had to be ground to finish size. The same heat treatment was given a duplicate bar in hydrogen. The bar treated in ammonia cracked on its surface when pulled as though case hardened; the hydrogen

bar did not; see Fig. 25. The structure of the NH_4 treated bar is shown in Fig. 26.

Charpy Bar Test.—The second sample, which contained 0.40 per cent. C and 3.50 per cent. Ni, was made up into Charpy impact test bars. One was heated to 850° C., cooled to 650° C., and treated with NH_3 at this temperature for 48 hr.; a second was treated the same way in nitrogen, and a third left untreated. They broke as follows: untreated, 180 ft.-lb. per sq. in., with dark fracture; in nitrogen, 168 ft.-lb. per sq. in., with dark fracture; in ammonia, 32 ft.-lb. per sq. in., with bright fracture. The broken ammonia-treated bar was ground off on the fractured end

FIG. 27.—CHARPY BAR AT FRACTURED END. 0.40 PER CENT. C., 3.50 PER CENT. NI. TREATED ABOVE CRITICAL CHANGE 48 HR. IN NH_3 AT 650° C. ETCHED 15 SEC. WITH 4 PER CENT. NITRIC ACID. × 25.

and polished and etched. The entire end is shown in Fig. 27, the light area being the area opposite the slot during treatment. This area is shown in Fig. 28; this grades off into the structure shown in Fig. 29, then Fig. 30, then Fig. 31, which last is characteristic of all the rest of the dark area. For brevity from here on these and similar structures will be referred to as austenitic, Fig. 28, martensitic, Figs. 29 and 30, Widmannstättian, Fig. 31. The martensitic area is rarely encountered spread out, as here, but usually is a very narrow zone, if it is visible at all. It always etches to a purplish color with nitric acid.

A third sample of 0.40 per cent. carbon and 2.50 per cent. nickel was used to make 60 Charpy bars. Of these, 15 were treated 20 hr. in NH_3 at 700° C., first heating to 850° C. The rest were given the same heat

FIG. 28.—WITHIN LIGHT AREA OF FIG. 27; OPPOSITE NOTCH DURING TREATMENT AUSTENITIC. ETCHED 15 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

FIG. 29.—SAME AS FIG. 27; JUNCTION OF LIGHT AND DARK AREAS. MARTENSITIC. ETCHED 15 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

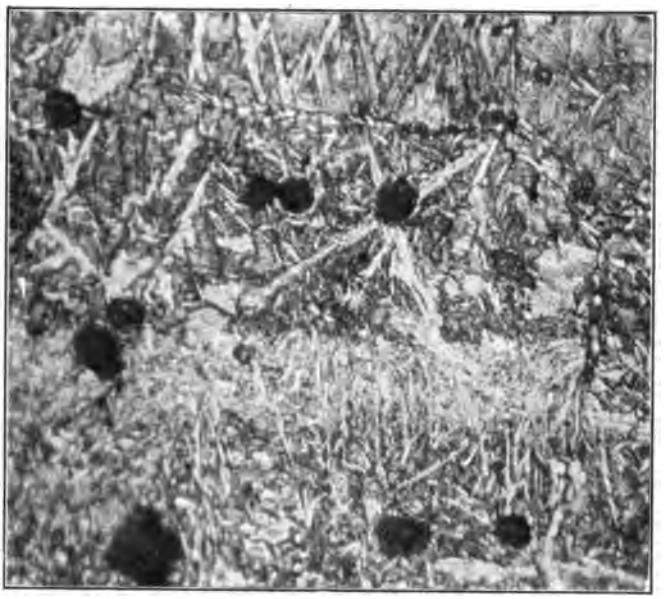


FIG. 30.—SAME AS FIG. 29; NEARER TO DARK AREA. MARTENSITIC. ETCHED 15 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

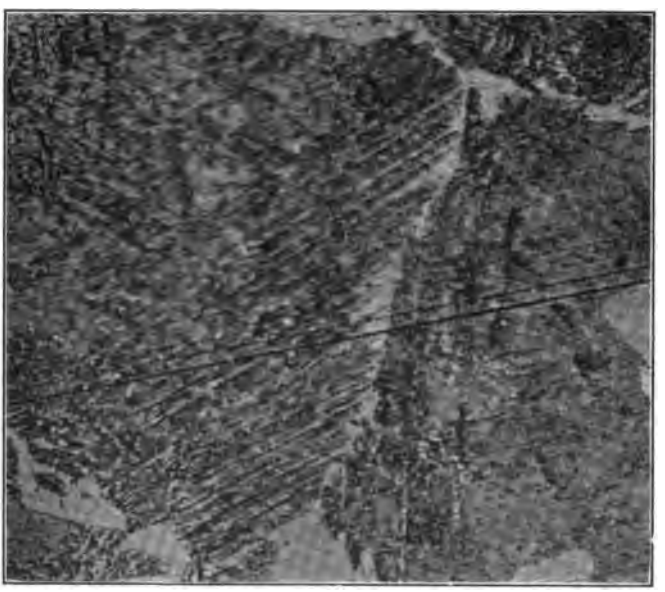


FIG. 31.—SAME AS FIG. 27; WITHIN THE DARK AREA. PROTECTED BY CONNECTING METAL DURING TREATMENT. WIDMANNSTÄTTIAN. ETCHED 10 SEC. WITH PICRIC ACID. × 500.

treatment in a box, sealed to exclude air. They were then broken in groups, according to location, one treated bar in each group, at various temperatures, by a method worked out in this laboratory in connection with another research, which will probably be described by its originators. Fig. 32 shows that the NH_3 treated bars are about evenly below the untreated bars and that this "nitrogen brittleness" is in no way affected by any narrow temperature range. Many of these bars, after breaking were polished and etched as in the first case. They show that with all conditions of time, temperature, flow, cooling, etc. kept as nearly the same as possible, there is still a great difference in the resulting structure. See also Figs. 33 to 39.

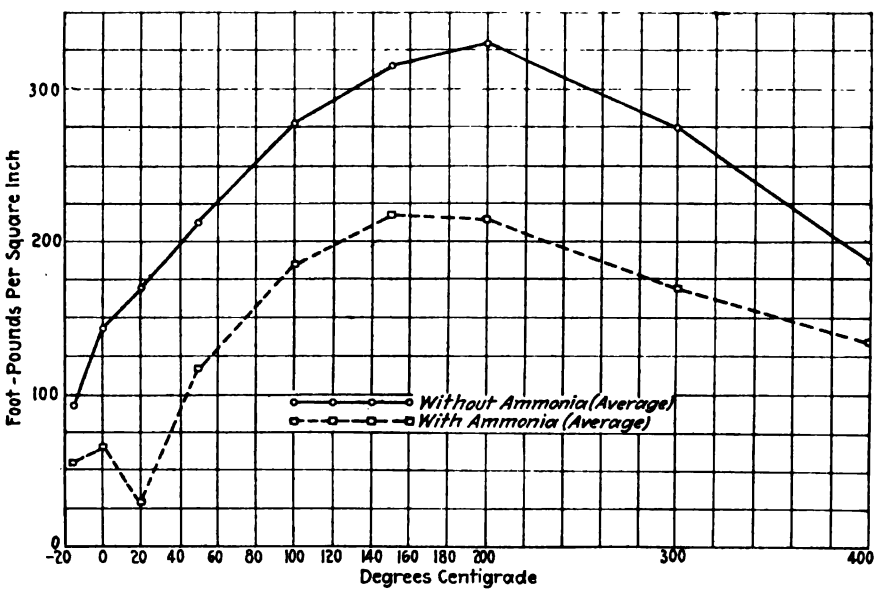


FIG. 32.—CHARPY TEST ON ANNEALED GUN STEEL.

The effect of a low draw on the austenitic structure is shown in Fig. 40, which is the same piece as is shown in Fig. 38, drawn for a few hours at 300° C. and repolished. Fig. 41 shows the same area as is shown in Fig. 28 after it was drawn for 24 hr. at 200° C.

The dark area after the draw is shown in Fig. 42. The "triangulation" is similar to that described by Doctor Langenberg.[6] In that case he attributed the formation to a critical rate of cooling through the Ar_1 range and supported his argument with experimental evidence. Here there is no critical cooling rate and the writer believes that the nitrogen content was sufficient to lower the Ar_1 range to a point where the steel was in a "critically mobile" condition to give this same effect.

[6] "Tests of Metals," 34. 1915.

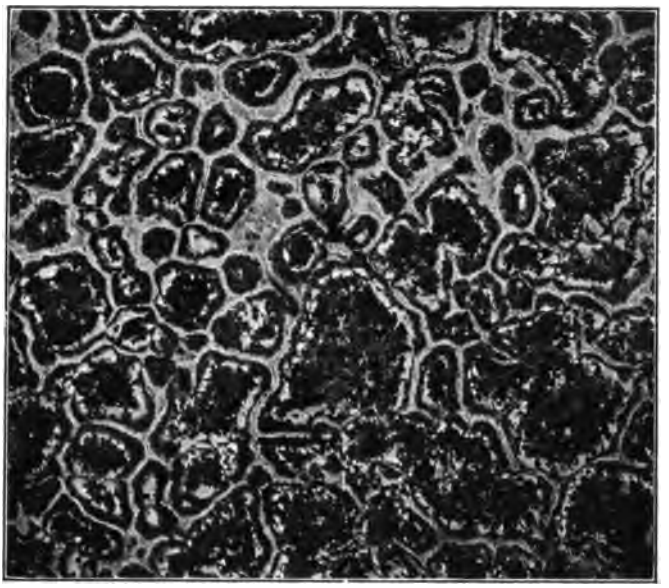


FIG. 33.—CHARPY BAR. 0.40 PER CENT. C., 2.50 PER CENT. NI. TREATED ABOVE CRITICAL CHANGE AT 700° C. FOR 20 HR. IN NH_3. BROKEN AT 100° C. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 50.

FIG. 34.—SAME AS FIG. 33. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

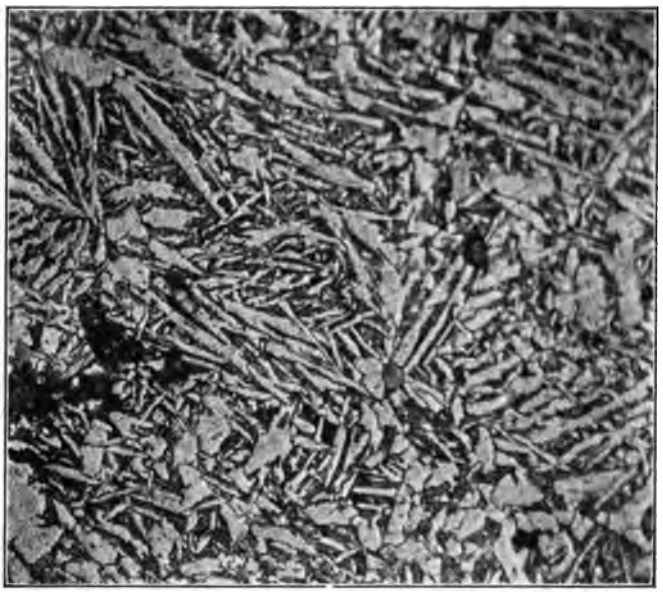


FIG. 35.—ANOTHER BAR TREATED AS FIG. 33, SAME COMPOSITION BUT BROKEN A 200° C. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

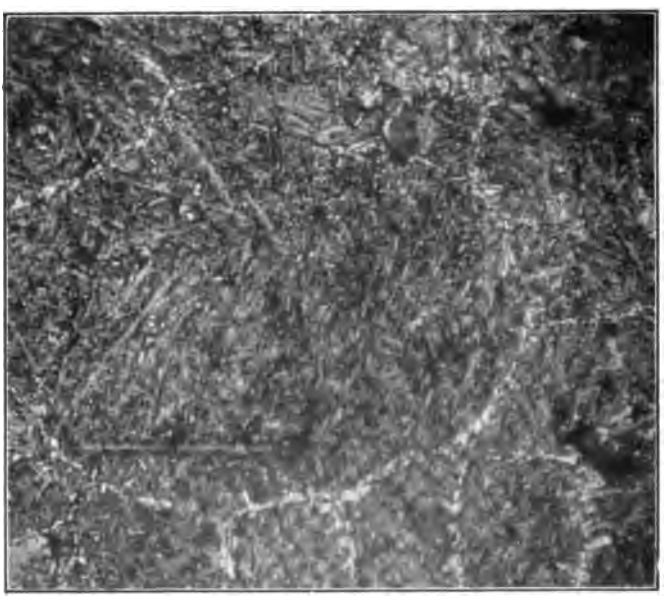


FIG. 36.—ANOTHER BAR OF SAME COMPOSITION AND TREATMENT AS FIG. 33. BROKEN AT 100° C. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

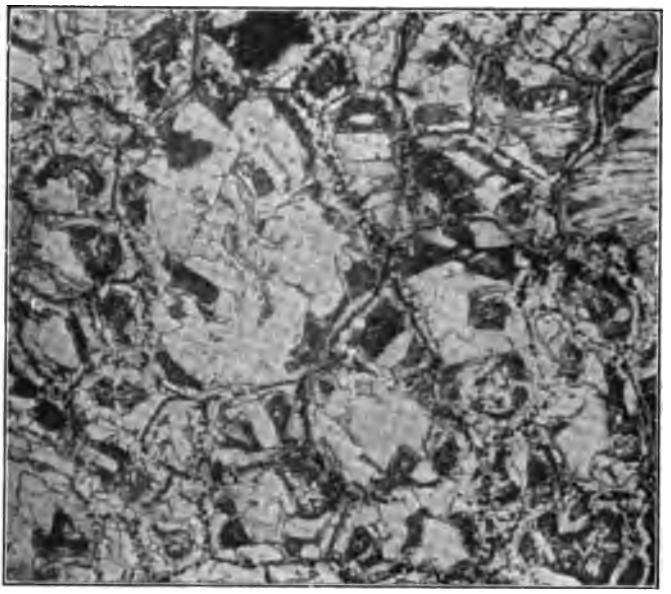


FIG. 37.—ANOTHER BAR LIKE FIG. 33, BROKEN AT 150° C. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

FIG. 38.—ANOTHER BAR LIKE FIG. 33, BROKEN AT 20° C. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

FIG. 39.—ANOTHER BAR LIKE FIG. 33; BROKEN AT 50° C. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

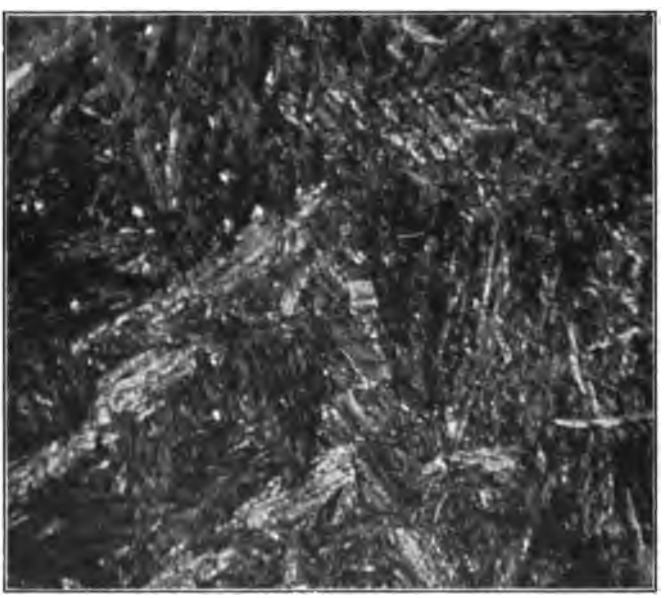


FIG. 40.—SAME AREA AS FIG. 38 AFTER DRAWING SEVERAL HOURS AT 300° C., SHOWING CHANGE FROM AUSTENITE TO MARTENSITE. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

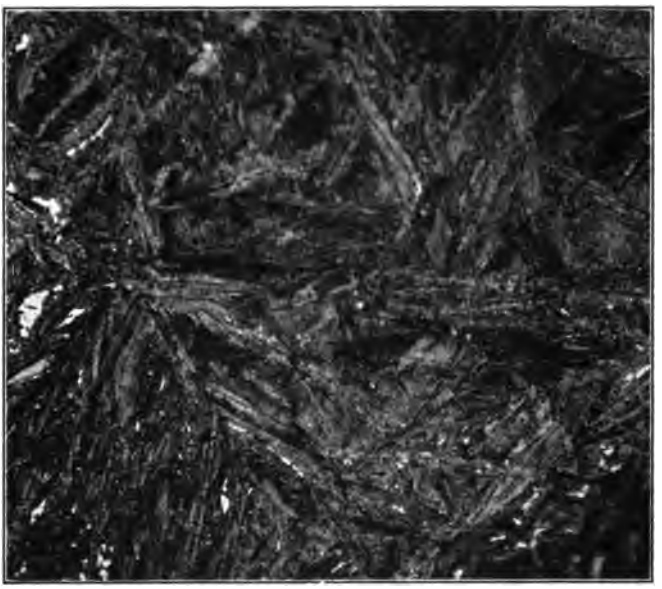


FIG. 41.—SAME AREA AS FIG. 28 AFTER DRAWING AT 200° C. FOR 24 HR. AUSTENITE IS CHANGED TO MARTENSITE. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 250.

FIG. 42.—IN SAME AREA AS FIG. 31 AFTER A 24-HR. DRAW AT 200° C. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

Other Alloy Steels.—The object of treating a large number of alloy steels 20 hr. in NH_3 at 650° C. and, in some cases, at 750° C. was to observe the depth of the case formed and gather an idea of the effect of the added element in retarding or accelerating this reaction. The method is far from quantitative. For instance, two steels, each of 0.40 per cent. carbon, 1.00 per cent. chromium, one of 0.20 per cent. vanadium, and the other of 0.25 per cent. vanadium, would not give in a half-dozen experiments consistent results as regards the depth of penetration. Such fine distinctions are beyond the scope of this method. It does, however, give a broad general idea of the effect of different families of elements. The

FIG. 43.—SAME AS FIG. 28 AFTER DRAWING 24 HR. AT 200° C. EXTREME OUTSIDE EDGE SHOWS NEW INTERCRYSTALLINE CONSTITUENT. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

writer does not feel that an elaborate exposition of the 300 or 400 experiments, each taking 20 hr. and many of them repeated several times, would be interesting. He will therefore briefly give only his observations.

With nickel and manganese, the case formed etches lighter than the normal metal and shows an austenitic appearance. With chromium, tungsten, molybdenum, uranium (and to a less extent with silicon, aluminum, and titanium), the case is darker after etching than the unaffected metal and the original structure remains visible. Silicon, up to 4 per cent., seems to have no effect on the depth of the case; and with low-carbon content, the piece is affected clear through showing no more resistance than a corresponding low-carbon steel low in silicon. Examples of light and dark cases are shown in Figs. 44 and 45. The curve is the bottom of the saw-cut.

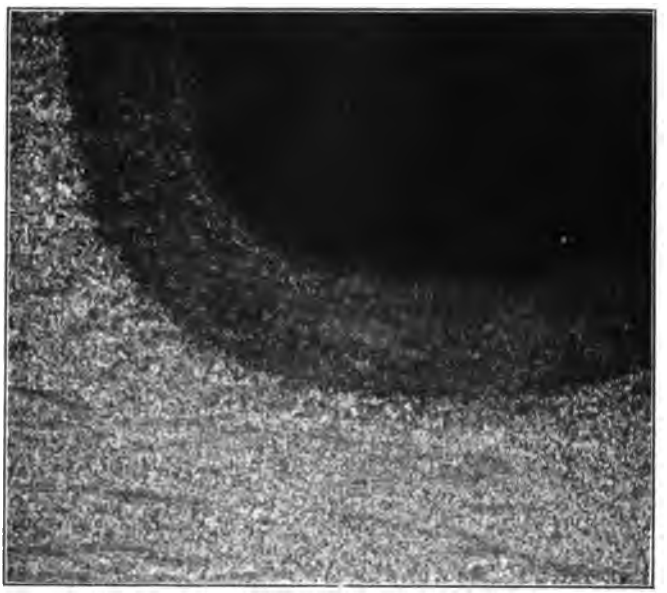


FIG. 44.—SAMPLE M1126A. 3 PER CENT. CHROMIUM, TREATED 20 HR. AT 650° C., SHOWING DARK CASE. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 50.

FIG. 45—SAMPLE 4011-7-A. 20 PER CENT. VANADIUM TREATED 20 HR. AT 650° C., SHOWING LIGHT CASE. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 500.

By far the most resistant of all steels tried was chrome-vanadium. The writer is uncertain just what part is played by the vanadium but it is possible that the effect is partly due to the texture it imparts to the metal. This method of investigation does not take account of the effect of grain size or porosity. With the cylinders in Part I, that was an important factor, as a cast cylinder lasted but a few days under pressure. This point could have been cleared up by some high-pressure experiments at the Carnegie Geophysical Laboratory, but as the work was about to be undertaken the use of the laboratory was withdrawn. As a substitute, Charpy bars have been made of all promising compositions and have been sent to Nitrate Plant No. 1 to be enclosed in the converter. There they will be subject to a volume-reducing pressure of $N_2 + H_2$ and a temperature of 500° to 600° C. for several months, then broken and examined for depth of case.

Hydrogen.—The effect of hydrogen has been ignored. The nascent H_2 from decomposed NH_3 is not as powerful a decarburizer as one might expect. Only in the case of hyper-eutectoid steel was it noticeable; and in very low-carbon samples, the carbon equilibrium swung in the other direction. The only case where hydrogen seemed to have played a part was the Charpy bar referred to above. The austenitic area in Fig. 28 after a 24-hr. draw in hydrogen showed a new constituent, as in Fig. 43; this looks like the solid solution that Andrews produced with hydrogen.

Heat treatment and hot work may influence the reaction, as the finely divided carbide goes into solution more readily than the massive carbide. However, it is also true that the gases do not penetrate the forged or heat-treated peices as readily as the casting, so the effects tend to balance. Any quenching treatment that tends to hold carbide in solution will assist the formation of the austenitic case, as might be expected.

Cold Work.—Cold work greatly assists the penetration, making it selectively faster on the cold-worked portions. This is easily demonstrated, as will be seen from Figs. 56 to 59, which will be discussed under the heading Erosion of Guns. Evidently the cold work produces a sort of mechanical amorphous mixture of cementite and ferrite, which changes to the solid-solution phase with nitrogen more easily than when distinctly crystalline. The amount of cold work needed to produce a noticeable effect is so slight that, at first, it was confused with strain. In the case of the ends of tensile bars that had been pulled and split in two along the axis and treated in ammonia, and again split along the axis and polished and etched, only the outside surface showed the white layer, and it became thicker toward the point of fracture. The white layer occurs only on the sides of the threads that took the stress of pulling.

TABLE 1.—*Containers from General Chemical Co.*

	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.	Phosphorus, Per Cent.	Nickel, Per Cent.	Chromium, Per Cent.	Vanadium, Per Cent.
Out, CS	1.06	0.26	0.174	0.029	0.013		0.65	
In, CS	0.58	0.23	0.169	0.030	0.015			
Out, S	0 35	0.35	0.017	0.049	0.020			
In, S	0.06	0.35	0.023	0.051	0.013			
Out, CVS	0 54	0.49	0.173	0.037	0.019		1.10	0.38
In, CVS	0.29	0.53	0.118	0.038	0.017		1.08	0.38
32-1	0.54	0.69	0.103	0.037	0.009		0.96	0.30
Out, NS	0.43	0.58	0.381	0.024	0.013	3.59		
In, NS	0.41	0.57	0.103	0.023	0.022	3.47		

TABLE 2.—*Containers from Bethlehem Steel Co.*

Number	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Sulfur Per Cent.	Phosphorus, Per Cent.	Nickel, Per Cent.	Chromium, Per Cent.	Vanadium, Per Cent.	Tungsten Per Cent.
4011-1	0.20	0.56	0.26	0.048	0.045				
2	0.40	0.93	0.45	0.035	0.046				
3	1.20	0.80	0.58	0.052	0.048				
4	0.65	0.25	0.33	0.045	0.034	2.00	2.13		
5	0.64	0.11	0.33	0.042	0.039	2.83	2.71		
6	0.38	0.62	0.20	0.049	0.045	1.46		0.16	
7	0.39	0.63	0.20	0.052	0.042			0.22	
8	0.35	0.63	0.20	0.048	0.047	3.08			
10	1.23	0.24	0.57		0.020				3.49
11	0.63	0.25		0.030			3.96	0.14	19.15
13	0.52	0.11	0.11	0.058	0.030				
14	1.30	0.08	0.08	0.030	0.016				
15	0.24	1.08	0.05	0.059	0.044				
16	0.50	1.08	0.10	0.060	0.032				
17	0.48	0.79	0.24	0 027	0.015		1.10		
18	0.54	0.80	0.48	0.026	0.016		1.14	0.27	
19	0.48	0.77	0.21	0.025	0.025		2.18		
20	0.46	0.67	0.14	0.027	0.014	3.49			
21	0.44	0.61	0.30	0.028	0.028	25.12	0.22	0.39	
22	0.33	0.49	0.16	0.046	0.028	3.25	1.44		
23	0.31	0.50	0.16	0.045	0.028	3.31	1.66		
24	0.32	0.56	0.16	0.043	0.028	3.37	1.28		
25	0.33	0.52	0.20	0.042	0.029	3.43	1.57		

The bronze container, No. 9, contained 0.12 per cent. manganese, 1.16 per cent. iron, 0.73 per cent. aluminum, a trace of lead, 32.70 per cent. zinc, 0.29 per cent. tin, 65 per cent. copper. The monel metal container, No. 12, contained 0.24 per cent. carbon, 1.71 per cent. manganese, 0.09 per cent. silicon, 0.02 per cent. phosphorus, 68 per cent. nickel, 2.52 per cent. iron, and 27.53 per cent. copper.

TABLE 3.—*Samples from the Bureau of Mines*

	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Tungsten, Per Cent.	Uranium, Per Cent.	Molybdenum, Per Cent.	Aluminum, Per Cent.	Titanium, Per Cent.	Vanadium, Per Cent.	Chromium, Per Cent.
SW13	0.38		0.14	4.48						
SW 3	0.56		0.30	1.99						
R 3	0.53					1.21				
R16	0.70				3.50					
1077	0.61	0.65	0.36		1.7					
1078	0.54	0.85	0.30		1.5					
1079	0.78	0.94	0.48		1.0					
1080	0.34	0.58	0.25		0.3					
1081	0.53	0.60	0.31		0.8					
1082	0.38	0.62	0.44		1.90					
1084	0.44	0.51	0.42		1.40					
1085	0.35	0.56	0.24		1.20					
1086	0.47	0.39	0.17		0.10					
1087	0.47	0.75	0.28							
U 4	0.43	0.68	0.63		0.31					
U 6	0.52	0.62	0.19		0.41					
U 7	0.53	0.63	0.29		0.04					
U 8	0.60	0.77	0.40		0.37					
U 9	0.49	0.69	0.34		0.75					
U10	0.39	0.53	0.27		1.09					
U12	0.52	0.61	0.32		1.86					
U13	0.53	0.48	0.26		3.10					
1090	0.50	0.70	0.26				4.94			
1094	0.46	0.68	0.37				4.92			
1100	0.28	0.30	0.43					0.97		
1098	0.40	0.70	0.27					0.42		
1088	0.51	0.42	0.58			1.2				
1089	0.66	0.79	0.22			2.0				
1091	0.44	0.76	0.43			1.15				
1092	0.36	0.67	0.41			2.15				
1096	0.39	0.66	0.29			2.10				
1097	0.36	0.65	0.30			3.00				
1099	0.40	0.80	0.34					0.40		
1110	0.53	0.67	0.50					0.90		
1116	0.40	0.64	0.18					0.58		
1121	0.43	0.44	0.19						0.98	
1122	0.42	0.55	0.38						3.00	
1123	0.39	0.35	0.20						1.95	
1124	0.38	0.65	0.23							0.96
1125	0.44	0.61	0.14							2.01
1126	0.46	0.76	0.17							2.77
1127	0.58	0.74	0.17				2.30			2.30

TABLE 4.—*Samples Made by the Thermit Process*

Thermit Heat, Number	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Chromium, Per Cent.	Vanadium, Per Cent.	Titanium, Per Cent.
1	0.21			2.96	1.03	
2	0.56		1.27	4.10		
5	0.11	0.64	0.94			
7	0 06	0.26	1.25			
8	0.20	0.35	0.92			0.30
10	0.39	0.67	0.48	1.02		0.18

TABLE 5.—*Samples Made by the National Tube Co.*

	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.	Phosphorus, Per Cent.	Chromium, Per Cent.	Vanadium, Per Cent.
CVS 1	0.33	0.55	0.90	0.014	0.018	1.68	0.17
SV 1	0.21	0.58	1.02	0.013	0.026		0.15
SV 2	0.12	0.75	1.00				0.26
S 1	0.23	0.45	0.98			0.17	

TABLE 6.—*Unclassified Samples*

	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.	Phosphorus, Per Cent.	Chromium, Per Cent.	Vanadium, Per Cent.
32–1 T 3.....	0.54	0.69	0.10	0.037	0.009	0.96	0.30
Casting T 1....	0.45	0.21	0.21	0.046	0.028	1.51	0.46
Forging T 2...	0.50	1.67	0.32	0.027	0.013	1.01	0.28
Norway iron...	0.06						
Projectile cap..	0.20						
C 14.....	1.11	0.09	0.27			16.25	
2-in. pipe.....	0.13	0.47	0.009	0.026	0.027	0.03	

TABLE 7.—*Samples Made at Watertown Arsenal*

	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.	Phosphorus, Per Cent.	Chromium, Per Cent.	Vanadium, Per Cent.	Molybdenum, Per Cent.	Nickel, Per Cent.
4273	0.57	0.77	0.54	0.013	0.007	1.38	1.78		
C 308	0.24	0.52	1.56	0.043	0.012	1.35	0.35	0.66	
E 185	0.35								3.50

TABLE 8.—*Samples (Wa) Analyzed in Laboratory of Watertown Arsenal or Results (Zr) Furnished by Detroit Ordnance Office*

	Carbon, Per ent.	Manganese, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.	Phosphorus, Per Cent.	Nickel, Per Cent.	Molybdenum, Per Cent.	Cobalt, Per Cent.	Zirconium, Per Cent.	Chromium, Per Cent.
Zr 1	0.409	0.80	1.65	0.011	0.014	2.93			0.36	
Wa	0.44					2.59				
Zr 3	0.44	0.90	1.32	0.010	0.018	3.06	0.27	0.59	0.37	
Wa	0.42					3.56		0.00		0.67
Zr 5	0.398	0.84	1.22	0.031	0.018	3.34			0.28	0.88
Wa	0.36					3.72				0.187

The Charpy impact test bars contained 0.40 per cent carbon, 0.66 per cent. manganese, 0.205 per cent. silicon, 0.033 per cent. sulfur, 0.034 per cent. phosphorus, 0.06 per cent. chromium, 2.48 per cent. nickel.

EROSION OF GUNS

A study of the data on erosion shows that it has been customary to treat a comparatively small number of experiments with an intensive study of each, rather than to take the salient features from a larger number of experiments. The opportunity to take the latter course was presented during the war but, so far as the writer has been able to find out, no new facts regarding erosion were discovered by any of the governments participating. It is surprising to find that while almost all metals have been experimented with in so-called erosion experiments, only a very few have actually been tried in a gun; and even these have been tried only in a hit-or-miss fashion.

Definition

For the purpose of this article, erosion will be defined as the enlargement of the bore and obliteration of the rifling from any cause. Some of these causes are: The eccentric path taken by the projectile and the consequent pounding; the whip or vibration of long guns; the muzzle droop of long guns; mechanical wear or abrasion, from the passing of the projectile, gases, or unburned powder, etc.; protrusion of liners and consequent loss of metal within the bore; swelling of barrel (in small arms) due to lowering of elastic limit; cracking of bore surface due to the formation of a hard layer of low ductility. Only this last feature of erosion will be dealt with here. The others will be referred to only as they affect the formation or effect of the hard layer.

To describe it briefly, even after the first few rounds, there is a notice-

able hardening of the surface, which is selective in its formation. The microscope reveals it as a layer that remains bright on etching and exhibits no structure. The formation follows the driving side of the lands, preferentially, and eventually the entire land and groove and even the powder chamber and forcing cone are affected. The formation on the bearing surface of the land extends much farther down the bore than on any other point of the circumference. This layer is characterized by hardness and especially by its low ductility, so that it no sooner forms than it develops a network of fine hair-like cracks which make a characteristic pattern, the largest being in a plane perpendicular or parallel to the axis of the bore. The enlargement of these cracks, and the consequent roughening of the bore, is generally admitted to be one of the chief determining factors in the life of guns of large calibers.

Before offering new theories of the cause and for the prevention of the formation of this layer, some of the most generally accepted theories of erosion will be mentioned.

The Gas-leakage Theory.—This was the first theory advanced, and it is also the one most generally held today, although it is very largely discredited by those who have made a careful study of the question. This theory assumes that the hot gases rushing past the projectile, in the early stages of combustion before the copper band has become engraved to the rifling, cut away the metal both by mechanical action and by melting or even vaporizing the metal.

In support of this theory, the results of Vieille[7] are offered as proof. Vieille did not intend his results to explain the formation of the first cracking. He was willing to pass over that as perhaps due to carbon monoxide or something he did not understand. He accepted the cracks as inevitable and intended his work to have a bearing only on the enlargement of these cracks. This theory does not in any way account for the existence of the hard layer, its selective formation, or the cracks themselves.

A high-speed photograph of a mortar firing, the first of a well known series taken at Fortress Monroe, Va., is shown in Fig. 46. There is no gas escaping ahead of the projectile in this case and there certainly should be leakage in a short gun like a mortar, if ever there is. A distinction should be made between guns using fixed ammunition and guns in which the shell is rammed home. In the former, erosion is followed by gas leakage, surely, but it remains to be shown that gas leakage precedes erosion.

The fact that the lands erode faster than the grooves cannot be reconciled to this theory. In fact, in some cases, the lands have worn off and their location on the circumference has been worn down below

[7] M. Vieille: "Memorial des Poudres et Salpêtres," 1901, 1902.

the level of the grooves, so that they are reversed, the groove now being the land. The maximum leakage should occur in the groove, of course.

As for the other side of the theory, the melting and washing away of the metal, the writer wishes to ask if this is not hopelessly removed from the facts. When a closed bomb is fired and the entire charge caused to pass through a single vent, as in experiments of the Vieille type, no doubt the surface metal has time to acquire the temperature of the passing gases. In a gun, the heat of the entire charge is not centered on one small sur-

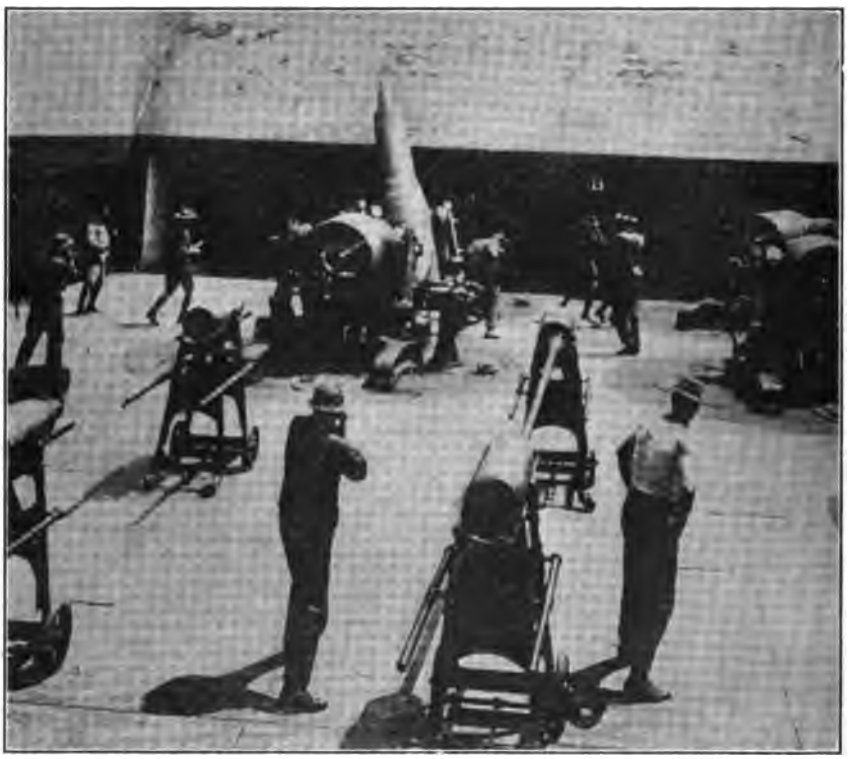


FIG. 46.—MORTAR FIRING; NOTICE SHELL LEAVING MUZZLE.

face. But taking this theory at its face value, see where it leads. The ideal gun would then be of platinum or any metal having a very high melting point. Howe[8] has pointed out carefully that the melting point cannot be the true measure of erodibility. He cites Vieille's table and shows that the density, specific heat and conductivity must all be taken into account. He might have used the term "diffusivity;" from the table, by F. T. Havard,[9] of this property, the following can be constructed.

[8] H. M. Howe: *Trans.* (1918) **58,** 513.

[9] F. T. Havard: "Refractories and Furnaces." N. Y., 1912. McGraw-Hill.

	Diffusivity	Melting Point, Degrees C.	Hardness	Erodibility
Aluminum	0.83	650	38	2200
Zinc	0.40	419	46	1000

Struck off to even comparative figures, this table becomes:

	Diffusivity	Melting Point	Hardness	Erodibility
Aluminum	2	3	19	2
Zinc	1	2	23	1

Aluminum is to zinc as $\frac{2}{1} \times \frac{3}{2} \times \frac{19}{23}$, or, approximately, as 5 is to 2 equals the expected relative resistance.

But zinc is to aluminum as 2 is to 1, by experiment, equals the actual relative resistance, which is an error of 500 per cent.

The fouling of the forward part of the bore is attributed to the molten or gaseous metal carried forward and deposited there. This fouling can be accounted for by the coppering of the bore in many cases and buckling of the liner in many more.

Cold-work Theory.—Another well-known theory is that the formation of the hard layer is due to cold work. This grew out of the work done by Professor Fay[10] when he was metallurgist at Watertown Arsenal. He showed that pieces of steel, when selectively cold worked, showed a formation of the white layer on the cold-worked areas. He could not explain this formation in the powder chamber of a gun, which is not cold worked, neither could this theory be reconciled with the martensite theory, so these results were discarded as probably due to coincidence, salience, etc. These results should not, and cannot be ignored, however.

Martensite Theory.—All who have studied the matter seem to agree on the martensite theory of erosion. This assumes that the thin skin of metal on the bore face is heated by contact with the combustion gases to a point well above the critical point, perhaps even beyond the melting point; that this thin skin is instantly chilled by the large mass of metal, causing martensite to form; and that each shot deepens the layer, minus what is carried away. In the first place, this layer is hard. The facts show that this layer is much more like austenite than martensite; but the facts had to be stretched considerably to account for martensite so austenite was hopeless.

It seems probable that the temperature of the bore face has been much exaggerated by assuming that there was time for equilibrium between the hot gases and cold metal. Take the case of the 75-mm.

[10] Henry Fay: *Trans.* (1916) **56**, 474.

field gun. It cannot be laid and fired, as in barrage work, faster than six times a minute. A gun fired at this rate for several hours is certainly in a state of thermal equilibrium and is radiating heat as fast as it gets it. When such a gun is suddenly closed up and the bore temperature measured, it is found to be from 200° to 250° C. Does it seem possible that even a thin layer was raised to 1000 or 2000° C. six times a minute for several hours?

The transfer of heat from hot gases to cold metal of containers is considered to take place principally by radiation. But it is also true that hydrogen under high pressure conducts heat almost as well as a metal. Even leaving convection out of consideration, it would seem that the

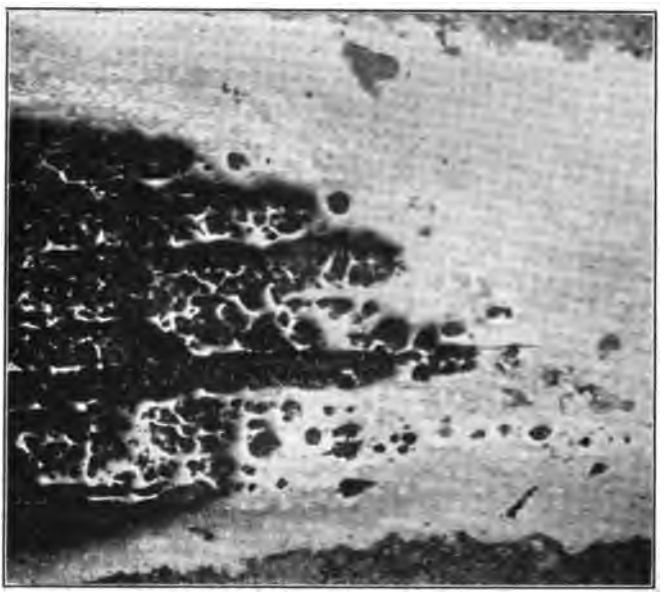


FIG. 47.—ROUGH GROOVE IN STEEL TREATED IN NH_3 AT 650° C. AND POLISHED, SHOWING FUSED APPEARANCE. × 50.

metal might reach quite a high temperature; that it does not is evidenced in several ways. It looks "fused" but this appearance can be produced at 650° C. with nitrogen and rough polishing; Fig. 47 shows an "artificial" eroded groove.

Also, it has never been pointed out that the ferrite network extends well into this hard layer. Fig. 48 shows a case of this on a plane perpendicular to the axis and Figs. 49 and 50 show this network on a plane perpendicular to a radius. The sharp outline of the original ferrite pattern is also shown. Could this metal have been above the critical point even for an instant, granting that pearlite would "merge" more readily than massive ferrite?

FIG. 48.—ERODED GUN TUBE; SECTION PERPENDICULAR TO AXIS. SHOWING FERRITE NETWORK EXTENDING INTO WHITE LAYER. × 500. ETCHED 20 SEC. WITH PICRIC ACID.

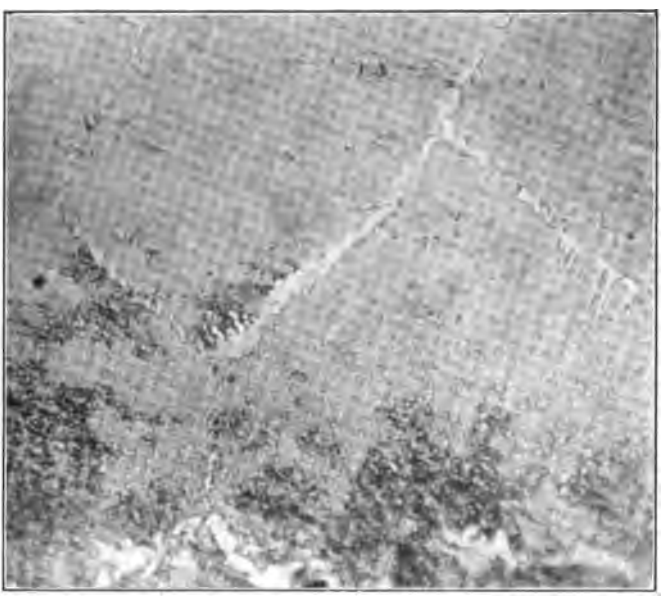


FIG. 49.—ERODED GUN TUBE; PLANE PERPENDICULAR TO RADIUS. SHOWING FERRITE NETWORK IN WHITE LAYER. × 500. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID.

Howe noticed the remarkable absence of cornices on the edge of cracks in the bore face; he explained this by assuming that the crack closed by heat, was flowed over with molten metal which solidified and then cracked open again on cooling. The writer wishes to offer the alternative explanation that the lack of cornices is due to lack of softening, that the metal is hard to start with and never gets hot enough to soften; in fact, that the start of erosion is really a shattering action such as you would expect in a glass-lined or enameled gun. The fact that the hard layer does not follow down the cracks can be explained by the simple assumption that the bottom of the crack, below the white layer, never

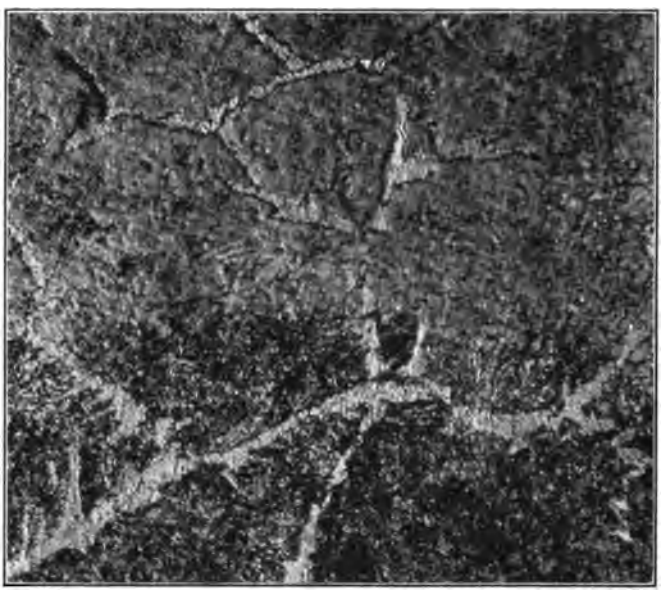


FIG. 50.—SAME AS FIG. 49 BUT TAKEN FROM A DIFFERENT GUN TUBE. × 500. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID.

gets warm enough for the formation to take place; also, it seems to be a strain effect, as will be mentioned under the heading Pressure. In some experiments described by Lieut.-Comm. H. E. Yarnell, U.S.N.,[11] a can was enclosed in a bomb in some cases. When it happened to be thrown against the vent, it was fused onto it; but in other cases this thin sheet metal was not fused by the heat of the explosion.

At this point it will be well to describe two other causes of erosion. When a machine gun is fired without water cooling, it can be brought to a yellow heat over the entire barrel, largely due to friction of the bullet. The erosion, if it may be so called, in this case takes the form of swelling and the bore increases in size several calibers until the bullets can pass

[11] H. E. Yarnell: *Jnl.* Soc. Naval Eng. (May, 1910) **22**.

through it sideways, in extreme cases. Here the contributing factor of erosion due to the white layer is at a minimum. Also, in certain thin liners, notably in the 75-mm. gun, the liner both protrudes and rotates. The protrusion is equivalent to removing that volume of metal from the bore and in effect constitutes erosion. Incidentally, the strain due to rotation at one end is often great enough to exceed the elastic limit of the steel of the liner.

NOTE.—In this connection, it perhaps has never been brought to general attention that the rotation and protrusion of liners is so often proportional in the same natures and calibers.

In the 75-mm. gun, in every case that has come to the writer's notice, the protrusion and rotation were numerically equal, no doubt a peculiar feature of the dimensions of the gun. Still this proportionality suggests that perhaps rotation, from the shell, is the cause of protrusion. By rotation is meant the relative rotation of

FIG. 51.—WHITE LAYER EXPOSED IN AN ERODED GUN TUBE ON A PLANE PERPENDICULAR TO A RADIUS. × 2. ETCHED 5 SEC. WITH 4 PER CENT. NITRIC ACID.

the muzzle end in respect to the breech. This assumes that torsion below the elastic limit of a hollow tube would lengthen and make it of smaller diameter. It is well known that torsion above the elastic limit will do this, and an immeasurably slight change in diameter would allow the liner to slide forward in the taper quite a distance as the ratio is 1000 to 1. An attempt made by the writer to show some slight elongation in torsion below the elastic limit was not wholly successful. The tendency was there indicated but the measurements were hardly within the accuracy of the instruments at hand.

Therefore the erosion due to the white layer is of varying importance in different natures and calibers and in lined and solid guns; it would seem to reach its maximum importance in a large rifle. This has been mentioned in some detail because it is the practice of the Department to test new steels for their resistance to erosion by firing in machine-gun or 75-mm. liner tests. Either method is cheap, but the liner will fail physically in a certain number of rounds, regardless of the actual erosion of the steel; that is, by being protruded and rotated. The machine gun, even with water cooling, is distinctly an extreme case of sustained fire. The residual temperature of one shot is added to the temperature rise

due to the next shot, giving a cumulative effect that far outweighs the temperature effect of the same number of rounds well spaced in time. It is safe to predict that no new steel will be found that is startlingly resistant in large guns as long as these methods of experiment are used.

Nitrogen Theory of Erosion.—The writer wishes to offer the suggestion that the hard white layer of an eroded gun is a locally cold-worked austenitic case due to penetration of nitrogen. Since nitrogen under pressure and with heat penetrates and combines with steel as has been described, it would be strange indeed if the reaction did not occur in the bore of a gun where there is an atmosphere of from 35 to 45 per cent. nitrogen, very hot and fresh from combination of another sort, *i.e.*, nascent and under a pressure of 30,000 to 45,000 lb. per sq. in. Since even molecular nitrogen has been shown to react at 500° C. and 1500 lb. per sq. in., the reaction must occur in a gun. By assuming that the white layer on the inside of a gun is the same as that which can be produced by nitrogen, most of the loose ends of previous theories are picked up. For that reason, and more especially because it offers a way out, this idea is offered for consideration.

Pressure

The significant pressures above would be the partial pressures due to nitrogen alone in the gun; 10,500 to 20,250 lb. per sq. in., and in the synthetic ammonia cylinders 375 lb. per sq. in. The time, of course, is very short in the gun, and the temperature of the metal itself is probably not more than a red heat. The work of P. W. Bridgman[12] has shown that steel will alloy with mercury under pressure when the pressure strain is such as to increase the volume of metal or, in other words, to make the metal more porous. The same pressure with a volume decreasing strain gives no alloying effect. The writer would not care to state that strain is a critical condition for the alloying of nitrogen with steel under pressure until he had tried it, but it seems evident, from the synthetic ammonia cylinder referred to above, that the strain has a great deal to do with the depth of the penetration. In Fig. 1, the effect of the indentation where the threading began was very slight, the strain at this point would be very little greater than at a corresponding depth in the solid metal. The plain steel cylinder showed the same effect and both showed that some definite temperature is needed, as the connections, which were somewhat air cooled, were not affected at all.

Hardness

The objection might well be raised that great hardness is not characteristic of austenite. But like all solid solutions (and pure metals) this constituent is very susceptible to hardening by cold work The impor-

[12] P. W. Bridgman: *Proc.* Amer. Acad., **46**, 323.

tance of the hardness of this layer seems to have been very much overestimated. Its low ductility is, of course, the main feature as far as erosion is concerned. In a gun the hardness by scleroscope is from 30 to 65; readings as high as 75 have been produced in the artificial white layer by cold work. There is much similarity between Figs. 1 and 51. Is it conceivable that a heat and chill effect could end so abruptly, bearing in mind that this is a picture of the layer cut at a very sharp angle to its surface, that is, on a plane perpendicular to a radius? Fig. 52 shows the junction of the two zones on similar sections; the sharpness is even more marked at 25 diameters. Fig. 53, at a magnification of 500, shows a radial section drawn 5 hr. at 300° C.

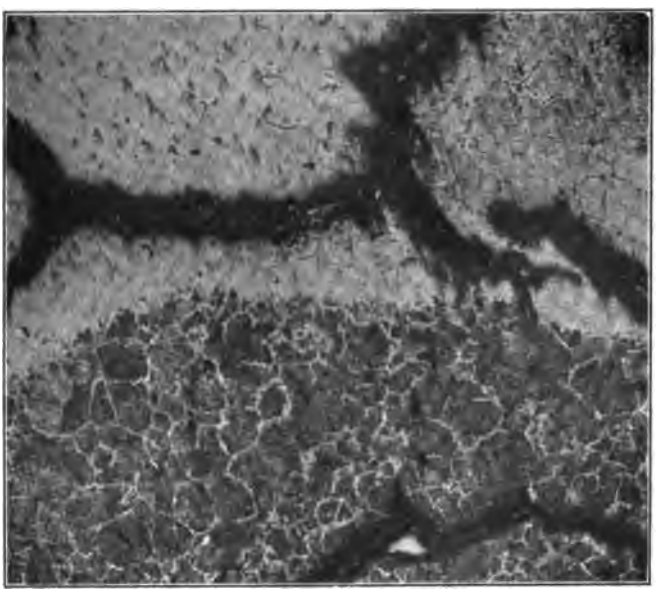


FIG. 52.—JUNCTION OF TWO ZONES, SAME VIEW AS IN FIG. 51. × 25. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID.

Howe pointed out that when the layer was heated to 1000° C. it disappeared, showing that it was due to unstable equilibrium due to chill. The writer has felt that there was also the possibility that at 1000° C. the high concentration of nitrogen in this layer was lowered by diffusion into the piece.

If a gun-tube section is etched with copper chloride, as in Fig. 54, the ferrite is clean. If heated to 1000° C., furnace cooled, and etched again with copper chloride, the ferrite is darkened, as in Fig. 55, giving the reverse pattern. This would seem to indicate that the nitrogen diffuses evenly through the austenite and, when it comes down, is found mostly in the ferrite.

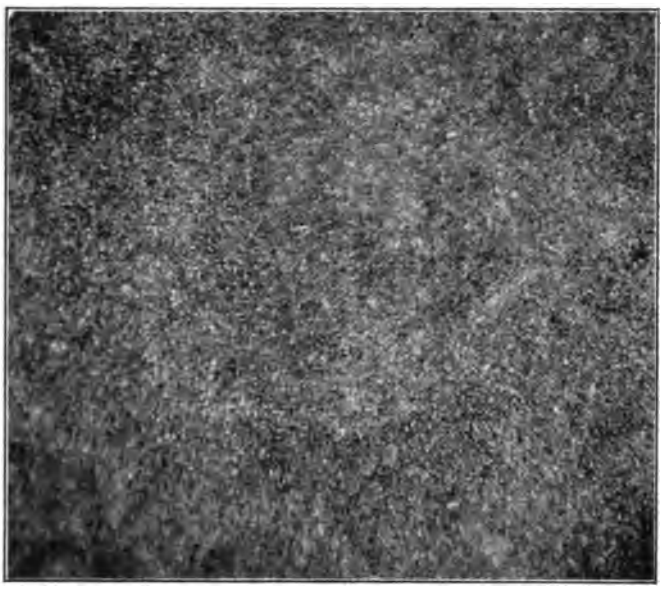


FIG. 53.—WITHIN WHITE LAYER. SAME SECTION AS IN FIG. 51 AFTER DRAW IN H AT 300° C. FOR 5 HR. × 500. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID.

FIG. 54.—ERODED GUN TUBE AREA IN NORMAL STRUCTURE. FERRITE LEFT LIGHT AS IN ANY STEEL. × 500. ETCHED WITH CUPRIC CHLORIDE.

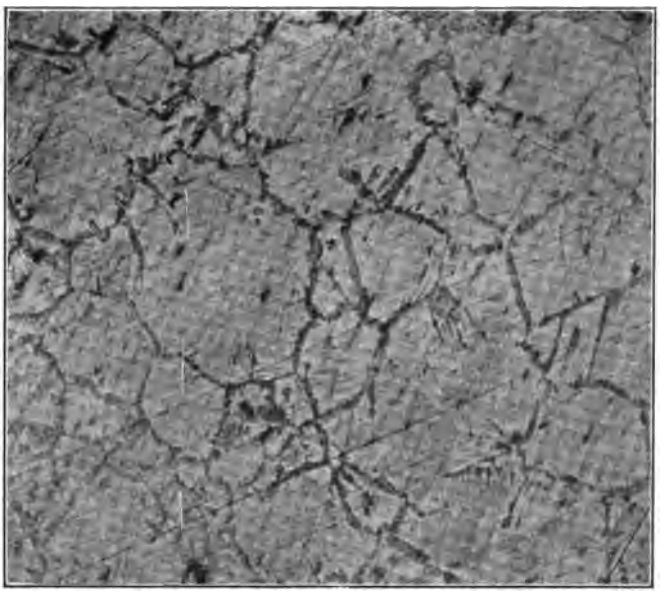


FIG. 55.—SAME AS FIG. 54. AFTER HEATING TO 1000° C., THE FERRITE NOW TAKES THE COPPER. × 50.

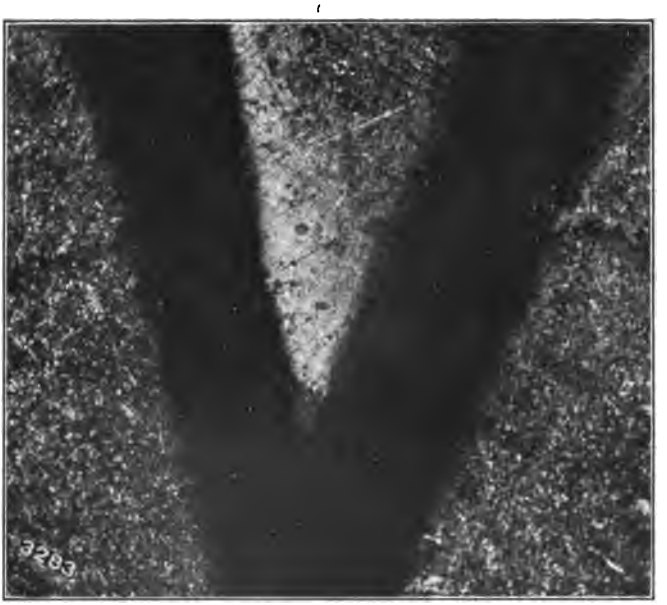


FIG. 56.—FAY'S A, FORMED BY STAMPING LETTERS AT AN ANGLE INTO A PRESSURE PLUG; AFTER FIRING 200 ROUNDS, POLISHED AND ETCHED. × 50.

The Cannon Section of the Engineering Division of Ordnance became interested in this work and authorized the manufacture of a liner for a 75-mm. gun out of chrome-vanadium steel. This seems an unfortunate selection, because a liner for a 75-mm. gun will fail for other reasons in a certain number of cases as shown above. The unpublished reports of the Cannon Section show that a test made in 1914 on machine-gun barrels of all usual gun steels and some unusual steels showed chrome-vanadium steel to rank first. In the case of a machine gun, the white layer is present but of not much importance, so that a chrome-vanadium steel gun of some large caliber might be expected to do very well.

FIG. 57.—LETTER V STAMPED AT ANGLE INTO SMALL PIECE OF STEEL TREATED IN NH_3 AT 650° C. FOR 4 HR.; POLISHED AND ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID. × 50.

Fig. 56 is a reproduction of one of Professor Fay's photographs; this was produced by actual firing. The results shown in Fig. 57 were formed in the ammonia furnace. The similarity is not perfect, of course, the high pressure in one case making the effect slightly different. It shows, however, that the action is selectively faster on the portions that have suffered plastic deformation. Fig. 58 is the thread of a tension bar split in two before treating; only the side that took the pull is affected, if the experiment is discontinued in time; also, only the outside of the contracted portion of the bar is affected.

In looking for steels that resist this penetration, it would seem evident that they must be of such composition as to resist the formation of the

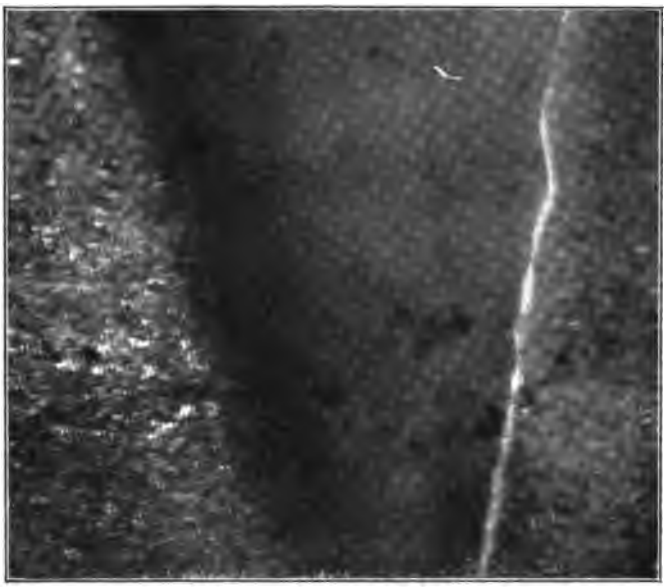


FIG. 58.—CROSS-SECTION OF THREADED PORTION OF SPLIT PULLED TENSILE BAR TREATED IN NH_3 AT 650° C. FOR 6 HR. ONLY SIDE OF THREAD WHICH TOOK PULL IS AFFECTED. × 50. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID.

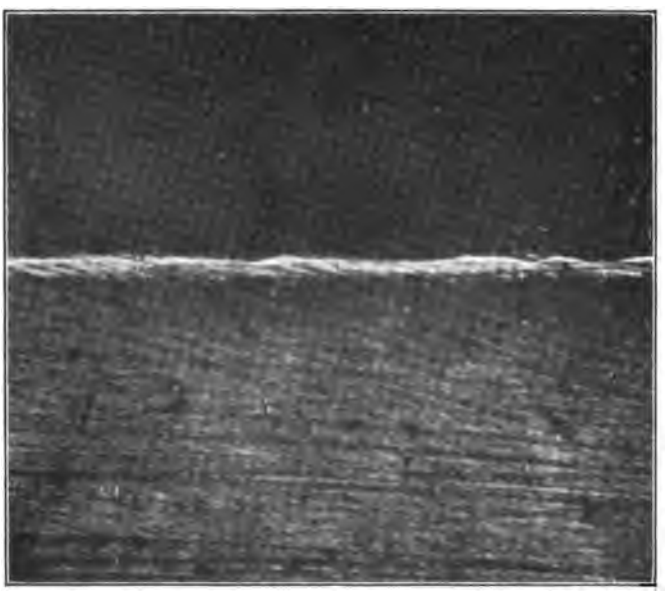


FIG. 59.—OUTSIDE EDGE OF BAR PORTION AS TENSILE BAR SHOWN IN FIG. 58 AT POINT NEAR FRACTURE. THE INSIDE SHOWED NO WHITE LAYER ALTHOUGH EQUALLY EXPOSED. × 50. ETCHED 10 SEC. WITH 4 PER CENT. NITRIC ACID.

solid-solution phase (chromium, etc.) and at the same time must be as little penetrable to gases under pressure as possible. A means of measuring this penetrability would be extremely desirable.

Some apology seems necessary for the large number of expressions of opinion herein which are not sufficiently supported by experimental evidence. In a few cases this might be done for those who are interested. But for the most part probability was sought for to the sacrifice of elaborate proof and the results are offered not as a completed research but in the hope that they may be of some interest to those now working on similar problems.

ACKNOWLEDGMENTS

All vacuum work and gas analyses were performed by Lieut. E. H. Hemingway. All analytical results are by E. K. MacNutt of the Watertown Arsenal. Much of the manipulation was carried out by Pvt. H. E. Koch, whose enthusiastic assisrance is hereby acknowledged. The writer is indebted to the many members of the personnel of this laboratory, and to many prominent scientists of Boston and Washington, for suggestions, advice, and assistance. To Dr. F. C. Langenberg, in charge of the Testing Laboratory, the writer is indebted for unlimited support, suggestions, and assistance. Doctor Langenberg should not be considered as necessarily concurring in the statements contained in this article.

DISCUSSION

W. E. RUDER, Schenectady, N. Y. (written discussion).—Nascent nitrogen is undoubtedly present in large percentages, and with pressure and the temperatures attained it seems that a combination must be achieved; the nitride so formed would have the properties and characteristics found in eroded gun liners. If this theory is correct it should be capable of metallographic proof, as heat treatment should bring out certain characteristic structure.[13] The specimens the writer used in a recent set of experiments were pure iron, however, and it is quite probable that material containing 0.40 to 0.60 per cent. carbon would show somewhat different structure. With alloy and carbon steels, the grain is usually so much finer that the characteristic needle structure might be overlooked in ordinary observation.

Mr. Wheeler takes strong exception to the association of the name iron nitride with the characteristic needles and dark patches found in N-bearing steels. As the writer is partly responsible for this name, he wishes to repeat the statement that in so far as our present knowledge of their actual chemical constitution goes, there is no evidence to justify the calling of these micrographic constituents iron nitride. The name

[13] *Chem. & Met. Eng.* (March 3, 1920) **22**, 403.

was used for convenience, mainly, and as it is truly descriptive and distinctive its continued use is justified until such time as a better name can be given.

The presence of carbon is not necessary for the formation of nitride needles and certainly they are not necessarily associated with any critical carbon content, as suggested by the author, rather they are caused by a certain nitrogen content, and then only on comparatively slow cooling.

Carbon may be associated with the "pearlite-appearing" areas, but micrographic evidence points to the assumption that the "lines and needles" are a true iron-nitrogen compound, while the patches are a binary eutectic (Fe_2-N-Fe?). Its appearance resembles "Steadite."

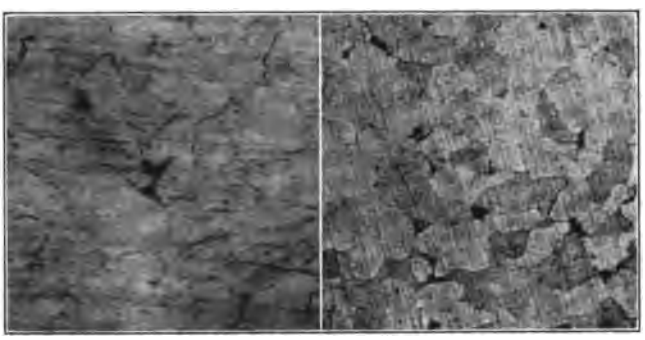


FIG. 60. FIG. 61.

FIG. 60.—ELECTROLYTIC IRON, NH_3, 700° C., 14 HR. ETCHED WITH NITRIC ACID. × 75.

FIG. 61.—SAME AS FIG. 60, ETCHED WITH STEAD'S REAGENT.

The author's statement (p. 301) that the outer nitride layer diffuses into the ferrite on heating agrees with the experiments covered by the first set of micrographs given herewith.

Due to the similarity between nitrogen-bearing areas and pearlite on nitric acid etching, it became desirable to find a method for distinguishing between them. Heat tinting gave some promise, as nitride needles and areas were colored differently from ferrite or pearlite. Ferrite containing small amounts of dissolved nitrogen colored more rapidly than pure ferrite. The distinctions were slight, however, between the nitride areas and pearlite, so a more certain method was sought.

Dilute HCl colored the nitride a deep black, while affecting pearlite to a less degree. As the distinction was not definite enough, copper-bearing solutions were experimented with; Stead's reagent, as used for the determination of phosphorus, was found to give entirely satisfactory results. The same care must be exercised as in testing for phosphorus, as too long an application covers the pearlite as well as the ferrite, and

the distinction between these is lost. The nitride, however, continues to etch black when in the eutectic or needle form. If dissolved in the ferrite it has the same effect as phosphorus with this reagent. The

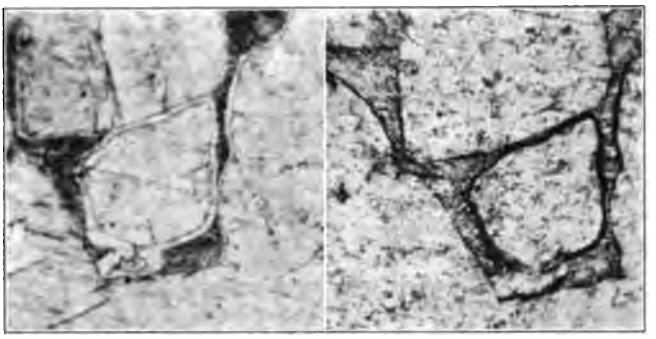


FIG. 62. FIG. 63.

FIG. 62.—ELECTROLYTIC IRON, NH_3, 700° C., 14 HR. ETCHED WITH NITRIC ACID. × 220.
FIG. 63.—SAME AS FIG. 62, ETCHED WITH STEAD'S REAGENT.

solution was made up as follows: Cupric chloride, 5 gm.; magnesium chloride, 20 gm.; hydrochloric acid, 10 c.c., alcohol (95 per cent.) to make up to 500 c.c. Absolute alcohol gave less satisfactory results.

The photomicrographs, Figs. 60 to 63, 66 and 67, of ammonia-treated electrolytic iron, etched with nitric acid and Stead's, respectively, show

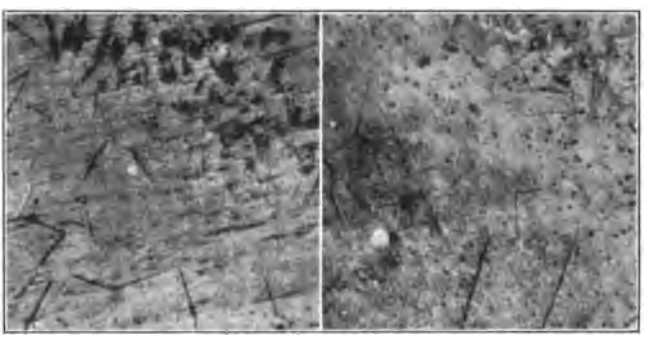


FIG. 64. FIG. 65.

FIG. 64.—ELECTRIC WELD ETCHED WITH NITRIC ACID.
FIG. 65.—SAME AS FIG. 64, ETCHED WITH STEAD'S REAGENT.

characteristic structures. With HNO_3 etching, the nitride's areas are usually edged with a hard white cementite-like constituent, which also forms part of the interior area. When etched with Stead's, this white constituent is eaten out, giving the deep black appearance shown in Figs. 61 and 63. Cementite areas remain entirely unaffected, and true

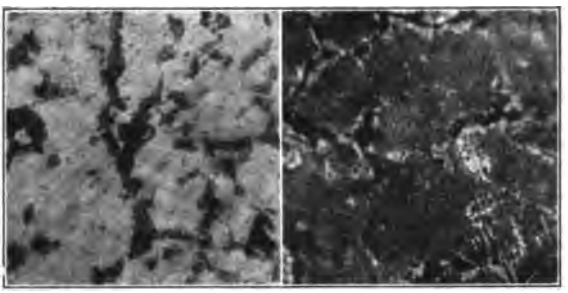


FIG. 66. FIG. 67.

FIG. 66.—IRON PIPE, NH_3, 700° C., 36 HR. ETCHED WITH NITRIC ACID. × 200.
FIG. 67.—SAME AS FIG. 66, ETCHED WITH STEAD'S REAGENT.

pearlite is not copper-plated, while ferrite is coppered. This makes it possible to distinguish between the other constituents present in the same specimen. The dark areas in Fig. 64 are pearlite and nitrite. Apparently the dark areas in Fig. 66 are mostly nitride, with which some pearlite is associated, as is shown by the use of Stead's reagent, Fig. 67.

The iron nitride, whether in massive, eutectoid, or needle form, is dissolved out by this reagent, while carbon-bearing constituents are unaffected, and ferrite is copper-plated.

GEORGE F. COMSTOCK,* Niagara Falls, N. Y. (written discussion).—This paper brings out some interesting facts regarding the effect of

FIG. 68. FIG. 69.

FIG. 68.—NITROGENIZED CAST STEEL, ETCHED WITH NITRIC ACID. × 400.
FIG. 69.—NITROGENIZED SHEET-BAR STEEL, ETCHED WITH NITRIC ACID. × 400.

*Metallurgical Engineer, Titanium Alloy Mfg. Co.

nitrogen in steel, and the author's theory regarding the erosion of guns seems the most reasonable that has been advanced. Some aspects of the author's metallographic conclusions, however, seem open to criticism. Work done by Ruder, Miller, and the writer has shown definitely that there is in the metal deposited in fusion welds, a metallic constituent that is capable of assuming different forms after heat treatment, and that is not a carbide but must contain nitrogen in some form. To call this constituent iron nitride may be unwarranted, but the name is convenient and descriptive and should be permissible with the understanding that no definite formula or chemical purity is implied. This constituent occurs in iron practically free from carbon (0.04 per cent. C and electrolytic iron); Figs. 68 and 69 show the same needles in a cast

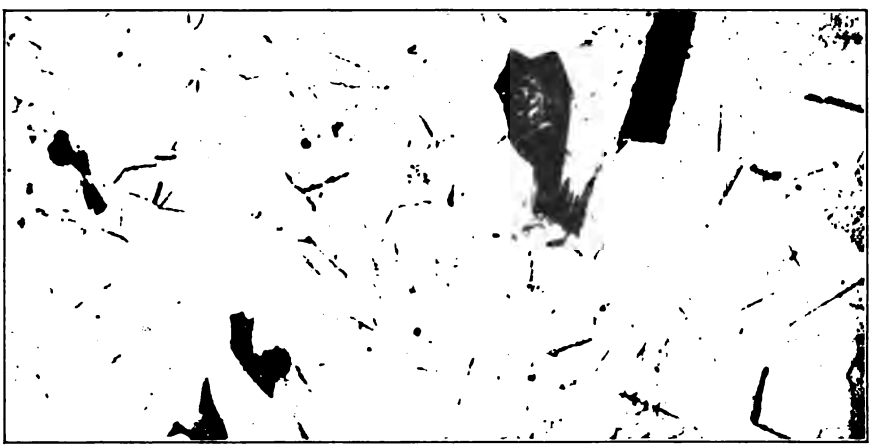


FIG. 70. FIG. 71.

FIG. 70.—SAME AS FIG. 68, BUT ETCHED WITH SPECIAL CUPRIC-CHLORIDE REAGENT.
FIG. 71.—SAME SPOT AS FIG. 69, BUT ETCHED WITH SPECIAL CUPRIC-CHLORIDE REAGENT.

steel of over 0.20 per cent. carbon, and in a sheet-bar steel of about 0.12 per cent. carbon, both specimens having been nitrogenized by heating in a cyanonitride compound. Hence this constituent does not seem to be associated with some critical carbon content, as suggested by the author.

Etching with nitric acid or picric acid will not distinguish between the constituents due to carbide, such as pearlite, etc., and those due to nitride, in a polished section of steel. Nitride may occur in steel in a form closely resembling pearlite and no simple metallographic method of distinguishing these constituents has so far been published. Through a suggestion of Doctor Ruder, a solution has been developed in this laboratory that will make this distinction in most cases. Fig. 70 shows the same specimen as Fig. 68, etched to darken only the nitride constituent, leaving the ferrite and the pearlite unattacked. Fig. 71 shows

the same spot as Fig. 69, repolished and etched like Fig. 70. The reagent is made up by dissolving 0.1 gm. $HgCl_2$ and 0.1 gm. $CuCl_2$ in 20 c.c.conc.

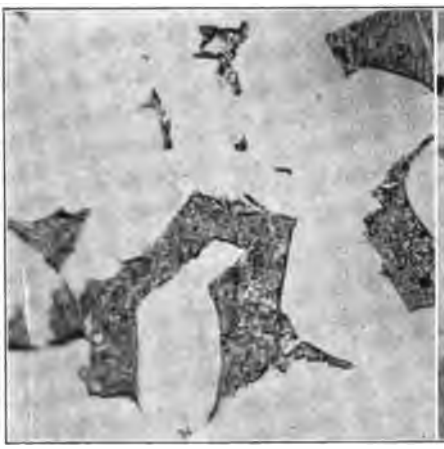


FIG. 72.

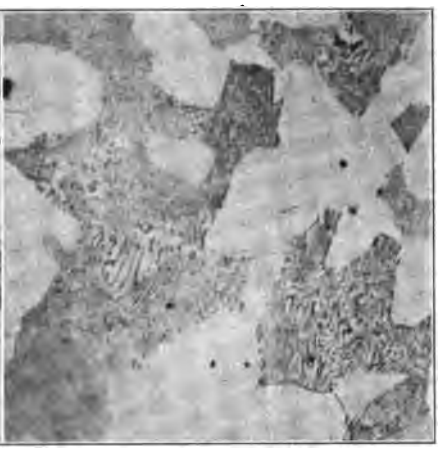


FIG. 73.

FIG. 72.—NITROGENIZED ELECTROLYTIC IRON, ETCHED WITH SPECIAL CUPRIC-CHLORIDE REAGENT. × 400.

FIG. 73.—SAME AS FIG. 68, BUT ETCHED WITH FERRICYANIDE REAGENT.

HCl and adding 80 c.c. of 95 per cent. ethyl alcohol. This is dropped on the polished surface and darkens the nitride constituent, but if the

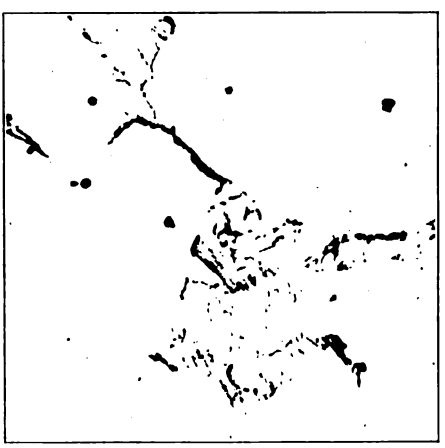


FIG. 74.—SAME SPOT AS FIG. 69, BUT ETCHED WITH FERRICYANIDE REAGENT.

etching is continued too long the pearlite or ferrite may become brown. The brown stain can be polished off and, by repeated etching and polishing, the nitride constituent may be blackened while the pearlite and ferrite are left bright.

Fig. 72 shows a specimen of nitrogenized electrolytic iron etched less deeply by the same solution. The dark patches, which looked like pearlite when etched with nitric acid, are a eutectoid form of the nitride constituent, and are not left bright by cupric chloride as pearlite would be.

In some cases a massive form of the nitride constituent was not attacked by the reagent described, so that such particles could not be distinguished from cementite, which often occurs in annealed low-carbon steel. The specimens were therefore boiled for from 10 to 30 min. in a reagent made up by dissolving 10 gm. potassium hydroxide and 1 to 4 gm. of potassium ferricyanide in 100 c.c. of water.[14] Massive cementite is blackened by this treatment, and pearlite and sorbite are turned quite brown, while the nitride constituent either is not attacked or is given a slight yellow stain. Fig. 73 shows the same specimen as Figs. 68 and 70 etched in this way, and Fig. 74 shows the same spot illustrated by Figs. 69 and 71, etched like Fig. 73.

By the use of these two solutions, a definite and sure distinction can be made in the metallography of steel between the constituents due to nitrogen and those due to carbon. The formulas given represent the results of a large amount of work with different solutions on various specimens, some of them known to contain nitride and others known to contain carbide. For the accomplishment of most of this work the writer is indebted to Austin B. Wilson. In view of the additional evidence here offered as to the identification of the nitride constituent by means of the new reagents, it would seem that its existence and the fact of its having been found in nitrogenized iron and steel fusion welds could no longer be questioned.

H. L. MERRING,* Washington, D. C. (written discussion).—The author's point is well taken in regard to the method of occurrence of nitrogen in iron and steel; that is, that at present we are not justified in calling the typical needles iron nitride. If iron nitride decomposes above 450° C. (and one author puts its temperature of decomposition as low as 200° C.), the metal would not be sufficiently plastic below that temperature to permit the iron nitride to form and migrate to the cleavage planes. I believe that the needles are associated with some critical carbon content.

W. E. Ruder[15] has given a review of the literature and the results of some investigations on a vacuum-fused electrolytic iron nitrogenized in what he calls pure ammonia, from which results he argues that the

[14] T. Murakami: Note on the Structure of Iron-carbon-chromium Alloys. *Jnl.* Iron and Steel Inst. (1919) **100,** 447.

* Lieutenant Commander, U. S. Navy.

[15] *Chem. & Met. Eng.* (March 3, 1920) **22,** 399.

needles are iron nitride and have nothing to do with the presence or absence of carbon. He apparently did not analyze for carbon but speaks of pearlitic appearing patches near the edge, which may be pearlite perhaps containing nitrogen. He shows a photograph at high magnification of a similar patch in a weld in steel which does not exhibit a true pearlitic structure but a martensitic appearance. Might this not be attributed to the presence of nitrogen and perhaps to the rate of cooling? He found in his nitrogenized iron sample that the needles appeared and disappeared on heat treatment, a temperature of 700° C. and slow cooling being necessary to cause their reappearance.

Giolitti's theory of the crystallography of alpha and beta iron might be applied to this problem. In Fig. 13, the edge of this sample, which showed 0.40 to 0.90 per cent. carbon, appears to contain a considerably greater proportion of ferrite than would be expected in steel of this carbon content. Where can the carbon be except dissolved in the ferrite either as carbon or carbide held in solution by the nitrogen? This agrees with Andrew's results as quoted on pages 262 and 269.

Agreeing with Giolitti that the crystalline habit of beta iron is massive and that of alpha iron platelike, and that the beta grains tend to form on the low-carbon areas in the original austenite as nuclei, is it unreasonable to suppose that the larger part, if not all, of the dissolved carbon is in the alpha needles? This being granted, as we recede from the edge and the percentage of total carbon drops, and more beta and less alpha iron come down, the proportion of carbon to iron in the alpha needles increases until they are reduced to needles of cementite containing nitrogen; Fig. 13 agrees very well with this explanation. The pronounced Widmannstättian structure at the edge fades away gradually to the typical needles, and it is not incompatible with Ruder's results, provided one grants (as he does not) that his sample contains carbon.

Mr. Wheeler's theory of the erosion of guns is the most practical to date and will merit a most thorough investigation. I see no reason to question the assertion that nitrogen renders steel austenitic in the cold and there is no doubt that the surface hardness of austenite can be greatly increased by cold working.

J. S. VANICK,* Washington, D. C. (written discussion).—While at ordinary temperatures nitrogen is generally an inert gas, at the temperatures at which the author's experiments have been conducted (650° C.), nitrogen, evolved from its compounds, is a vigorously active element.

The term iron nitride is apparently substituted in discussions of the structure for the sake of brevity and convenience. The author says that a stable compound (FeN_2) forms in treating iron with ammonia. That this compound, in its free state, decomposes at 450° C. need not discredit

* Metallurgist, Fixed Nitrogen Research Laboratory, American University.

its occurrence in solution in iron even at temperatures up to the melting point. Recent progress in the study of fusion welds and of iron exposed to ammonia gas adds to our knowledge of the structural appearance of compounds of iron, carbon and nitrogen. Hydrogen is an accessory in the case of ammonia saturations and oxygen is an accessory in the process of welding. The similarity of the structure resulting from the reactions, in each case establishes the presence of a compound of iron and nitrogen formed by the absorption of nitrogen in the iron. The fact that such a compound does occur makes the item of molecular composition of secondary importance.

Since nitrogen combines with iron to form a compound that, under certain conditions of heat treatment, appears similar to the iron-carbon eutectoid (pearlite), it is difficult to waive the probability of residual nitrogen remaining in solution and accept the substitution of non-decarburization or the re-appearance of hidden carbide. Would a complex compound of carbon, iron, and nitrogen release its nitrogen upon heating in vacuo at 1000° C. and leave a carbon-iron residue? If such were the case, the pearlitic areas of Fig. 11 are not sufficiently extensive to represent a steel containing 0.58 per cent. carbon, neither are they similar to the structure of nitrogenized Norway iron, containing 0.64 per cent. carbon. An explanation of the difference might be found if decarburization in the former case were more fully considered.

Heating in vacuo at 1000° C. would induce decarburization as well as denitrogenization. In the absence of specific data in relation to denitrogenization, it is difficult to form a connection between Figs. 5, 7, 11, and 12 that would support denitrogenization accompanied by the appearance of pearlite rather than decarburization accompanied by the occurrence of a pearlitic appearing nitrogen compound. In view of this possibility, the analysis of the specimens helps in the solution of the problem. The table of carbon determinations given appears to justify, to a great extent, the proclamation of decarburization.

Figs. 14 and 15 illustrate the tabular structure of iron-carbon-nitrogen compounds; it would be interesting to follow such a structure through the temperature-vacuum treatments.

The association of the erosion of guns with the nitrogenization theory, is worthy of further study. If a gun had a lining of very low carbon steel, the nitrogenization of the bore might be followed by the structural changes that have been so closely identified with the occurrence of iron-carbon-nitrogen compounds in steel. This method should survive, provided that the penetration by the gases exceeds the deformation by the shell. The perfection of sensitive analytical methods would likewise tend to provide a means toward obtaining decisive evidence.

O. A. KNIGHT, State College, Pa.—The Watertown Arsenal, some time before Mr. Wheeler was employed there, conducted an investigation of

the erosion of two 10-in. rifles.[16] At the conclusion of that investigation I was convinced that nitrogen played a rather important part in the erosion of guns although we did not feel that sufficient evidence was at hand to warrant advocating the nitrogen theory of erosion then. Later, Mr. Wheeler conducted this series of experiments, which seem to confirm the fact that nitrogen plays a great part. In the investigations which I have carried out since leaving the Arsenal, I find that the surface layers produced by this nitrogen treatment are extremely brittle and extremely fragile; therefore in guns the physical forces that exist would readily sweep this layer away.

A study of Figs. 19 and 45 would indicate that the specimens were not mounted before polishing for microscopic examination, or that any precaution was taken to prevent any of the surface layer being chipped off during the grinding and polishing.

On page 286, he states: "The object of treating a large number of alloy steels 20 hr. in NH_3 at 650° C., and in some cases at 750° C., was to observe the depth of the case formed and gather an idea of the effect of the added element in retarding or accelerating this reaction. The method is far from quantitative. For instance, two steels each of 0.40 per cent. carbon, 1.00 per cent. chromium, one of 0.20 per cent. vanadium, and the other of 0.25 per cent. vanadium, would not give in a half-dozen experiments consistent results as regards the depth of penetration. Such fine distinctions are beyond the scope of this method. It does, however, give a broad general idea of the effect of different famil iesof elements."

In my investigations I found it absolutely essential to mount all specimens in a low melting-point alloy before polishing in order to retain the extremely brittle outside surface layers; then an even uniform case will be formed when steels of similar composition are given the same ammonia treatment. At least this holds for plain carbon steels, from a very low per cent. carbon to considerably above the eutectoid per cent.

Every specimen that was not mounted before polishing showed the same irregular cases as Mr. Wheeler's. I therefore believe the conclusion quoted to be in error.

J. W. Richards,* South Bethlehem, Pa.—The rapid erosion of guns was of great interest during the war and undoubtedly it will be the subject of interesting investigations until the reasons are found. If this nitrogen compound is decomposable at a low temperature, its rapid decomposition may effect a surface change in the iron or steel.

[16] Report of Tests of Metals, etc., at Watertown Arsenal for year ending June 30, 1917, 245.

* Professor of Metallurgy, Lehigh University.

O. A. KNIGHT.—I do not believe the nitrogen compound is as easily decomposed as we might think. After steel has been heated in ammonia for several hours, it is possible to decompose the compounds formed by heating them at the same temperature in hydrogen. It takes, however, a much longer time to bring back the normal structure by the hydrogen treatment than it does to impart the structure by the ammonia treatment. The same length of time in hydrogen gas will not completely remove the nitrogen or eliminate the structure that was formed. Annealing at considerable lengths of time does not decompose the compounds very rapidly.

H. E. WHEELER (author's reply to discussion).—I have been asked to describe what precautions were taken to prevent the surface layers from being chipped off during grinding and polishing. A few of the thin sections were mounted in clamps before grinding. Most of the samples treated in ammonia were not so mounted, the shape of the sample making it unnecessary. Each piece was slotted with a saw cut before treating, and after treating the piece was cut in two perpendicular to this slot to expose a surface for examination. The "case" so formed was as uniform as the frame on a picture, and any chipping off could have been detected. As some of the samples showed marked change after a draw as low as 200° C., I do not think they should be mounted in alloy.

To repeat, my work led me to the conclusion that the iron-carbon-nitrogen system is not essentially different in its metallography from the iron-carbon-nickel system. I did not recognize nor identify the eutectic described by Doctor Ruder, but a eutectic is a very definite thing and if it can be produced in sample of iron free from carbon by analysis after treating, the iron-nitrogen system should be as clearly exposed as the iron-phosphorus system. Cooling curves of iron carrying varying percentages of eutectic from hyper to hypo would be very interesting. Surely iron nitride does not crystallize out without some heat effect. I am still uncertain whether the metallographic distinctions offered between this eutectic and pearlite do preclude the possibility of its being pearlite with nitrogen dissolved in the eutectic ferrite.

Effect of Sulfur and Oxides in Ordnance Steel

By William J. Priestley,* M. E., South Charleston, W. Va.

(New York Meeting, February, 1922)

In the manufacture of gun forgings and other steel parts that, in service, are subject to sudden high stresses and shocks, it is most desirable to use steel possessing the greatest toughness and ductility possible without sacrifice of strength. In order to obtain this condition, it is necessary to procure steel that shows the highest possible elongation and reduction of area without lowering the tensile strength and elastic limit. Proper heat treatment of the steel can control this condition within certain limits. When heat treatment has failed to produce the desired results, metallurgists have used steels containing molybdenum, zirconium, vanadium, chromium, tungsten, etc.

The purpose of this paper is to describe a method by which these desired physical properties may be procured—by the elimination of certain impurities that inherently exist in steel made by the open-hearth process, and without the use of expensive alloys.

Design of Gun Forgings

In the manufacture of gun forgings, a certain elastic limit is fixed by the designer, and the walls of the gun are made of the proper thickness, allowing a suitable factor of safety for the high stresses and sudden shocks that occur during gun firing. The elastic strength of the gun is about 1.4 times the stress set up at any point along the bore of the gun during firing with the maximum powder charge.

As the stresses set up in the walls of the gun during firing are mostly "tangential," all physical tests are taken in this direction. Due to the length of the forgings, these tangential test bars are always taken at right angles and transverse to the direction of flow of the metal in forging. Furthermore, test bars taken across the grain of the metal will more frequently expose defects and foreign inclusions in the steel than will bars

* Steel Superintendent, U. S. Naval Ordnance Plant.

taken in the direction of flow of the metal in forging. Impurities in the steel will also be more readily detected by transverse[1] test bars.

With a given tensile strength and elastic limit, a steel with higher elongation and reduction of area is more desirable for service where sudden stresses and great shocks are encountered. The high elongation denotes ductility and the high reduction of area denotes toughness; for the purposes just mentioned, these properties are preferable to a higher tensile strength and higher elastic limit with a lower elongation and lower reduction of area.

Results Obtained with Electric Steel

Some interesting results were obtained recently in the manufacture of heavy ordnance forgings at the U. S. Naval Ordnance Plant, South Charleston, W. Va. The steel was made by the duplexing process, in which cold charges of pig iron and scrap were melted in a 75-ton basic open-hearth furnace, where the dephosphorizing was done, and subsequently the deoxidizing and desulfurizing was done in two 40-ton basic-lined electric furnaces. A comparison of the physical results obtained from forgings made by this process with similar forgings made directly in an acid open-hearth furnace at the works of one of the leading industrial steel plants, noted for high-grade open-hearth steel, shows that the steel with the lower phosphorus and sulfur has the greater toughness and ductility. Transverse tensile test bars from electric steel, though having the same tensile strength and elastic limit as the bars from the open-hearth steel, have a much greater elongation and reduction of area.

The results given in Tables 1 and 2 were obtained on tangential tensile test bars. All forgings received a green annealing before machining; after machining they were quenched and drawn. For the results given in Table 2, it was impossible to procure comparative results from open-hearth or electric steel made in private industrial plants. The first impression on comparing these results is that the higher elongation and reduction of area are due to the low phosphorus and sulfur, as shown by the chemical analysis; all the other elements are approximately alike.

Effect of Phosphorus

It would be difficult to draw any comparison between the open-hearth and electric steel in regard to the phosphorus content. This element is in solid solution with the iron as a phosphide and the per-

[1] Tensile test bars referred to here as transverse are taken from the forging in such a manner that their axes are at right angles to the direction of flow of the metal in forging. In the specifications for gun forgings, bars of this kind are referred to as "tangential." The axis of a "longitudinal" test bar is parallel to the direction of flow of the metal in forging.

centages are too small in both the open-hearth and the electric steel to denote any difference even with a microscope. The lower phosphorus in the electric steel might have a slight effect on the elongation, due to producing a somewhat smaller grain and decreased brittleness in the steel.

Effect of Sulfur

It has been stated by a recognized authority on the manufacture of steel that "the effect of sulfur on the cold property of steel has not been accurately determined but it is certain that it is unimportant. In common practice, the content varies from 0.02 to 0.10 per cent. and, within these limits, it has no appreciable influence on the elastic ratio and the elongation or the reduction of area." This statement probably relates to commercial steels tested longitudinally. In this case the sulfur, in the form of manganese sulfide, has been drawn out into thin shreds in the direction of forging or rolling and is not so easily noticed in the results of longitudinal test bars as it would be in the case of transverse bars. With the overbalancing amount of manganese present in all the steels referred to in this article, probably no iron sulfide is present in the steel for none of the ingots showed any signs of tearing during forging. Steel containing iron sulfide is known to tear in forging and is termed "hot short" by steelworkers. Manganese sulfide has been described as being present in the ingot in the form of small globules between the grains of the metal. Having about the same fusing point as the metal, these inclusions become equally plastic when the ingot is heated for forging and are drawn out into long thin shreds—just as slag is drawn out in wrought iron. If, however, the amount of manganese sulfide present is not enough to form these globules, these shreds will not be developed in forging and transverse test bars will show as good results in elongation and contraction as longitudinal bars.

The following test bars were taken from a piece of steel resembling that shown in Fig. 3. Two of the bars were drilled longitudinal with the forging and the other two tangential. They were given exactly the same heat treatment, quenched at 1425° F., and drawn at 1200° F.; the results were as follows.

	Tensile Strength, Lb. Per Sq. In.	Elastic Limit, Lb. Per Sq. In.	Elongation, Per Cent.	Reduction of Area, Per Cent.	Fracture
Tangential	111,500	55,500	21.3	44.5	Silky lipped
Tangential	108,500	58,000	20.9	40.2	Irregular and woody
Longitudinal	109,600	58,500	24.1	55.8	One-half cupped silky
Longitudinal	109,400	59,700	24.1	56.3	Three-fourths cupped silky.

It will be noted that the tensile strength and elastic limit are practically equal in the tangential and longitudinal bars, but the non-metallic

TABLE 1

	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Phosphorus, Per Cent.	Sulfur, Per Cent.	Nickel, Per Cent.	Tensile Strength, Pounds Per Square Inch	Elastic Limit, Pounds Per Square Inch	Elongation, Per Cent.	Reduction in Area, Per Cent.
Forging, 16 in. diam. by 9 ft. long, 8½ in. bore; weight 5000 lb. Average results from 10 forgings (or 20 bars) of each class										
Open-hearth steel*	0.36	0.66	0.23	0.04	0.039	2.98	98,013	57,720	20.4	36.9
Electric steel	0.34	0.64	0.22	0.012	0.008	1.16	95,435	64,010	24.5	58.3
Physical requirements							80,000	50,000	21.0	30.0
Forging, 11 in. diam. by 28 ft. long, 7½ in. bore; weight 6000 lb. Average results from 10 forgings (or 40 bars)										
Open-hearth steel	0.37	0.65	0.21	0.040	0.044	3.02	104,785	73,162	19.6	39.4
Electric steel	0.30	0.67	0.179	0.012	0.009	2.81	96,995	67,785	24.2	55.9
Physical requirements							90,000	55,000	18.0	30.0
Forging, 9 in. diam. by 28 ft. long, 5½ in. bore; weight 4000 lb. Average results from 10 forgings (or 40 bars)										
Open-hearth steel	0.38	0.64	0.206	0.039	0.040	3.09	103,185	73,231	19.2	39.9
Electric steel	0.34	0.65	0.212	0.014	0.012	2.87	100,340	72,610	23.2	52.5
Physical requirements							90,000	55,000	18.0	30.0
Forging, 26 in. diam. by 2 ft. long, 5 in. bore; weight 4000 lb. Average results from 5 forgings (or 15 bars)										
Electric steel*	0.37	0.54	0.182	0.020	0.026	2.66	110,182	67,067	17.8	37.1
Electric steel	0.35	0.72	0.169	0.006	0.008	2.91	108,681	77,038	20.2	49.3
Physical requirements							95,000	65,000	18.0	30.0
Forging, 9 in. diam. by 28 ft. long, 5½ in. bore; weight 4000 lb. Average results from 10 forgings (or 40 bars)										
Electric steel*	0.39	0.53	0.16	0.020	0.025	2.65	95,245	64,979	19.3	37.0
Electric steel	0.34	0.64	0.21	0.014	0.012	2.87	100,340	72,610	23.2	52.5

* These ingots were made by a private industrial plant during the war.

TABLE 2

	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Phosphorus, Per Cent.	Sulfur, Per Cent.	Nickel, Per Cent.	Chromium, Per Cent.	Tensile Strength, Pounds Per Square Inch	Elastic Limit, Pounds Per Square Inch	Elongation, Per Cent.	Reduction in Area, Per Cent.
Forging, 17½ in. diam. by 28 ft. long, 10 in. bore; weight 12,000 lb. Average results of 10 forgings (or 40 bars)											
Physical requirements	0.36	0.72	0.224	0.014	0.009	2.90		98,225 90,000	67,777 60,000	25.0 18.0	55.3 30.0
Forging, 22 in. diam. by 11 ft. long, 16 in. bore; weight 6000 lb. Average results of 10 forgings (or 60 bars)											
Physical requirements	0.35	0.74	0.184	0.012	0.009	0.59		99,856 93,000	63,953 53,000	23.9 18.0	55.6 30.0
Forging, 22½ in. diam. by 11 ft. long, 17 in. bore; weight 6000 lb. Average results of 10 forgings (or 40 bars)											
Physical requirements	0.36	0.55	0.206	0.021	0.015	3.14	1.39	140,332 130,000	124,182 105,000	17.1 15.0	48.0 40.0
Forging, 24 in. diam. by 8 ft. long, 16 in. bore; weight 6500 lb. Average results of 10 forgings (or 20 bars)											
Physical requirements	0.35	0.75	0.214	0.012	0.008	0.52		100,195 93,000	64,875 53,000	24.0 18.0	53.9 30.0
Forging, 32 in. diam. by 2 ft. long, 18 in. bore; weight 4000 lb. Average results of 9 forgings (or 27 bars)											
Physical requirements	0.35	0.70	0.172	0.008	0.009	2.97		102,509 95,000	71,572 65,000	22.4 18.0	53.8 30.0

enclosures in the steel caused the tangential bars to show a lower elongation and lower contraction than the longitudinal bars.

Effect of Oxygen

There is nothing in the usual chemical analysis to show how much oxygen is present in steel. It exists in small amounts in even the best steel and has bad results. In large amounts, it produces tearing during forging or rolling, and when cold is brittle under shock. If present in steel, it is probably in the form of iron and manganese oxides and silicates. Oxygen is most prevalent in basic open-hearth steel. Where non-metallic enclosures are great enough to analyze, they have been reported to show the following composition: SiO_2 50 per cent., MnO 30 to 40 per cent. Al_2O_3 7 to 18 per cent., FeO trace. In the acid open-hearth furnace a more effective reaction between the slag and the steel tends to deoxidize the steel more thoroughly. This cannot be done completely on account of the air present in the acid open-hearth furnace.

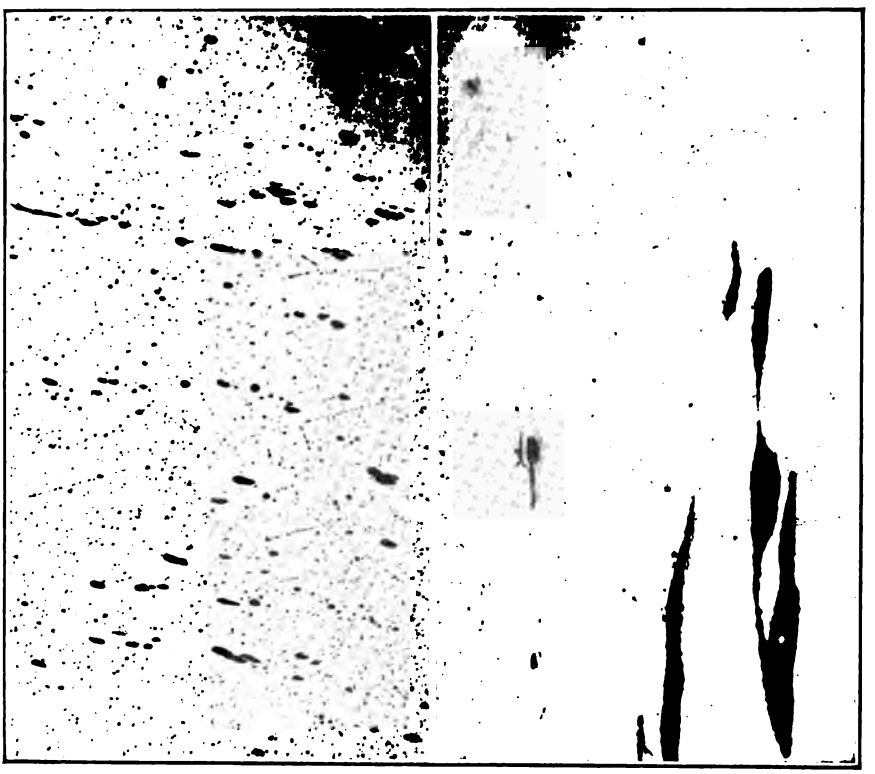
A condition exists in the basic electric furnace which cannot exist in the basic or the acid open-hearth furnaces. With a reducing atmosphere in the furnace, it is possible to form a calcium carbide slag free from metallic oxides; with constant rabbling of the bath, any oxides in the steel will rise to the slag, where they are reduced by the carbon present. The iron and manganese are returned to the bath, and the resulting carbon monoxide is liberated to the atmosphere of the furnace. Unless the slag and bath are free from oxygen, it would be impossible to maintain a carbide slag; and unless the slag and bath were thoroughly deoxidized, it would be impossible to retain the sulfur in the slag as calcium sulfide.

Hence, the conditions that bring about the elimination of sulfur from the steel guarantee that oxides and other non-metallic impurities have also been eliminated. This is demonstrated in the case of the last two forgings in Table 1. While the forgings were made by the electric refining process in different steel plants, the test bars of steels containing the higher sulfur show no better results than the forgings made by the acid open-hearth process. The photomicrograph of the electric steel with high sulfur, Fig. 3, reveals more enclosures than the electric steel with low sulfur.

Photomicrographs of Open-hearth and Electric Steel

Photomicrographs have been taken of bars picked at random from each of the three classes of steels described. The polished surface of these bars was parallel to the direction of forging. One set of photomicrographs was taken at 25 diameters, so as to include as many enclosures as possible and to show their distribution. A second set was

taken at 200 magnifications, to show the formation of the enclosures. It will be noted that the non-metallic enclosures in the steel with low sulfur and highest elongation and reduction of area are smaller than in the steel with higher sulfur content and the lowest elongation and reduction of area. All the enclosures in the low-sulfur steel seem to be of the same kind, whereas, in the acid open-hearth and electric steel with higher sulfur, there are two types—the small round ones and those that were



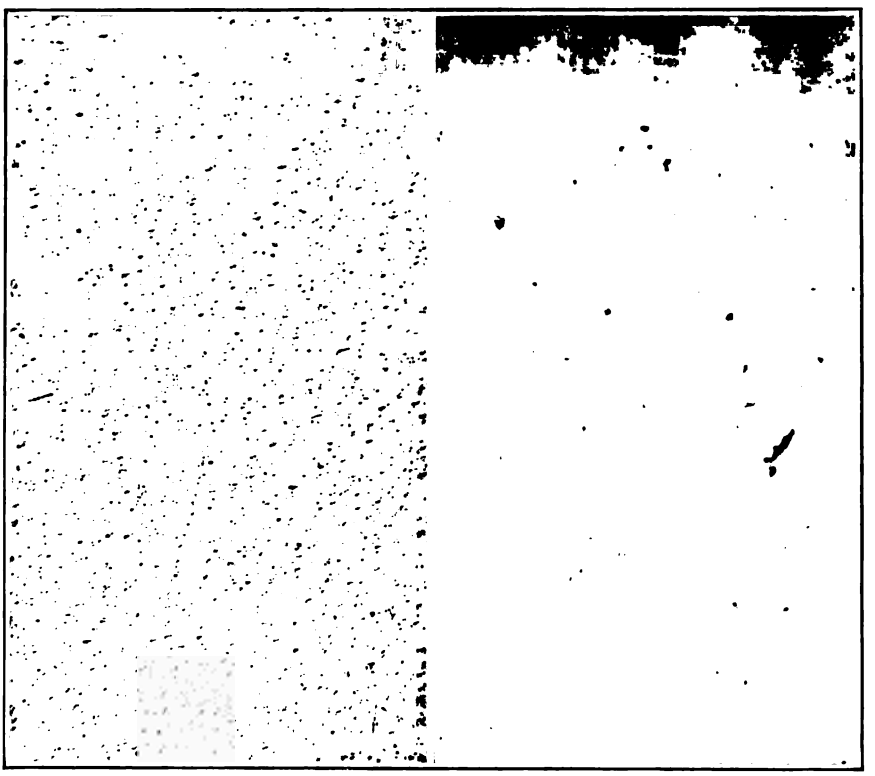
a *b*

FIG. 1.—ACID OPEN-HEARTH STEEL. *a*, UNETCHED, ×25; *b*, UNETCHED, ×200.

elongated and drawn out in forging. The light colored elongated enclosures in the acid open-hearth steel are probably a mixture of manganese sulfide, oxides, and silicates.

Fig. 1 shows a longitudinal section taken from an acid open-hearth steel forging 11 in. in diameter, 28 ft. long, 7½ in. bore, weighing 6000 lb.. having the following chemical analysis: Carbon 0.35 per cent., manganese 0.68 per cent., silicon 0.240 per cent., phosphorus 0.040 per cent., sulfur 0.053 per cent., nickel 3.00 per cent. Physical tests on tangential test bars gave the following results:

	Tensile Strength, Lb. Per Sq. In.	Elastic Limit, Lb. Per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.	Fracture
BM	101,700	75,600	18.1	36.8	Woody
BI	101,500	77,300	20.5	38.6	One-half cup woody
MO	96,800	65,200	18.1	32.4	Woody, streaked
MM	97,100	63,400	18.0	37.1	Irregular, woody
Required by specifications	90,000	55,000	18.0	30.0	

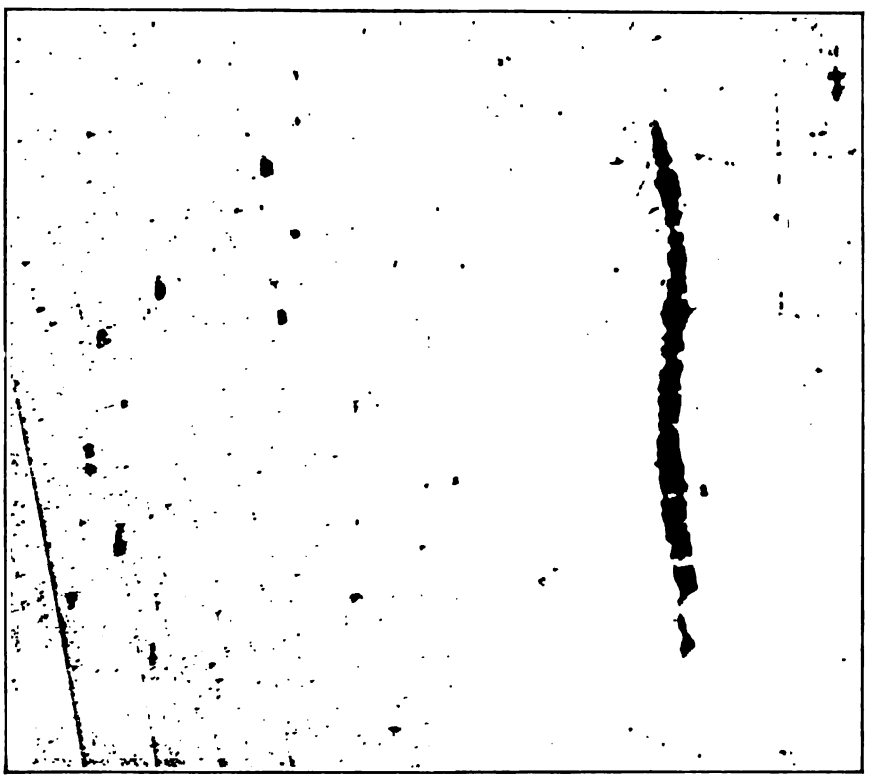


a *b*

Fig. 2.—Electric steel with low sulfur. *a*, Unetched, ×25; *b*, unetched, ×200.

This forging was green annealed at 1600° F., rough machined and quenched at 1450° F., and drawn to 1200° F. The elongated enclosures or shreds follow the direction of forging. A tensile bar taken transversely, or across, these enclosures will show a lower elongation and lower reduction of area than if these impurities were not present. No aluminum was added to this steel in the open hearth. This enclosure is much lighter than that in the electric steel. It did not pull apart in forging and appears to have been more plastic and probably contains more manganese sulfide than either of the other two specimens, Figs. 2 and 3.

In Fig. 2 is shown a longitudinal section taken from a low-sulfur electric steel forging 11 in. in diameter, 28 ft. long, 7½ in. bore, weighing 6000 lb., having the following chemical analysis: Carbon 0.28 per cent., manganese 0.74 per cent., silicon 0.140 per cent., phosphorus 0.011 per cent., sulfur 0.006 per cent., nickel 2.81 per cent. Physical tests on tangential test bars gave the following results:



a *b*

FIG. 3.—BASIC ELECTRIC STEEL MADE DURING THE WAR IN PRIVATE INDUSTRIAL PLANT. *a*, UNETCHED, ×25; *b*, UNETCHED, ×200.

	TENSILE STRENGTH, LB. PER SQ. IN.	ELASTIC LIMIT, LB. PER SQ. IN.	ELONGATION, PER CENT.	REDUCTION OF AREA, PER CENT.	FRACTURE
BM	92,800	67,700	26.4	64.5	One-half cup silky
BI	93,400	67,500	26.9	64.7	Silky lipped
MO	94,200	67,100	24.9	56.5	Silky
MN	97,400	72,900	23.8	54.9	Three-fourths cup silky
Required by specifications	90,000	55,000	18.0	30.0	

This forging was green annealed at 1600° F., rough machined and quenched at 1450° F., and drawn to 1190° F.

The elongated enclosures found in the acid open-hearth steel are lacking. Transverse test bars show high elongation and high reduction of area with no decrease in tensile strength and elastic limit. No aluminum was added to this steel in the melt shop.

Fig. 3 shows a longitudinal section taken from a basic electric steel forging 9 in. in diameter, 28 ft. long, 5½ in. bore, weighing 4000 lb., having the following chemical analysis: Carbon 0.41 per cent., manganese 0.48 per cent., silicon 0.168 per cent., phosphorus 0.026 per cent., sulfur 0.029 per cent., nickel 2.60 per cent. Physical tests in tangential test bars gave the following results:

	Tensile Strength, Lb. Per Sq. In.	Elastic Limit, Lb. Per Sq. In.	Elongation, Per Cent.	Reduction of Area, Per Cent.	Fracture
BM	93,100	61,900	21.1	44.7	Silky cup
BI	91,600	63,800	16.3	33.4	Woody shear
MO	90,000	61,900	23.6	45.0	Slightly woody
MM	90,300	64,300	24.2	45.3	Woody, crystalline
BID	90,100	62,100	22.5	42.0	Slightly woody
Physical requirements	90,000	55,000	18.0	30.0	

This forging was green annealed at 1600° F., rough machined and quenched at 1450° F., and drawn to 1220° F.

Elongated enclosures similar to those found in the acid open-hearth steel are equally prominent but not so numerous. They are darker in color and the fact that they pulled apart indicates that they are more brittle. These inclosures are probably silicates of iron, manganese or aluminum. From 4 to 6 oz. of aluminum per ton of steel was added to the bath in the electric furnace, on the end of a rabble iron, just before tapping.

Manufacture of Steel at Naval Ordnance Plant

From the foregoing physical results and substantiating data, it is evident that the presence of sulfur, oxides, and other non-metallic enclosures are detrimental to the ductility and toughness of steel. Where the best quality of steel is required, it is necessary to keep these impurities to a minimum. The basic open-hearth furnace eliminates the phosphorus but only slightly reduces the sulfur; the oxides must be eliminated by the addition of deoxidizers, such as ferromanganese, ferrosilicon, aluminum, etc., which are sometimes added to the open-hearth furnace and rabbled after the air is shut off, but more frequently are added to the metal in the ladle. If added in the ladle, the reactions are incomplete and the products of combustion remain suspended in the steel, forming harmful non-metallic inclusions. Gun forgings and other ordnance material, where transverse tests are required, have never been successfully made from basic open-hearth steel. The bars generally fail in elongation and reduction of area

tests, because of the presence of these inclusions. They generally break with a laminated and woody fracture.

The acid open-hearth furnace is better for making steel free from oxides and non-metallic impurities, and ordnance forgings have been obtained from acid open-hearth steel. While neither phosphorus nor sulfur can be eliminated in this furnace, the amount of these impurities may be kept down by the selection of high-grade scrap and pig iron. The oxides may be largely eliminated by the effective reaction between the slag and the steel.

The method of making steel at the U. S. Naval Ordnance Plant aims for the elimination of phosphorus, sulfur, and oxides. The metallic charge of the open-hearth furnace consists of 40 per cent. basic pig iron and 60 per cent. miscellaneous scrap, including turnings, crop ends, etc.; up to 8 per cent. of limestone is added with the charge and sufficient ore to lower the carbon to approximately 0.20 to 0.25 per cent., which is slightly below the amount required in the finished steel.

The pig iron has the following approximate analysis: Carbon 3.50 to 4.00 per cent., manganese 0.95 per cent., silicon 0.65 per cent., phosphorus 0.15 per cent. and sulfur 0.04 to 0.05 per cent. The crop ends are usually low in phosphorus and sulfur, being the discard from ingots made at this plant by the electric refining process. The miscellaneous scrap, consisting of boiler plate, punchings, and turnings, averages approximately 0.04 to 0.05 per cent. phosphorus and sulfur.

The limestone shows the following analysis: SiO_2 1.43 per cent., Fe_2O_3 + Al_2O_3 0.60 per cent., $CaCO_3$ 97.54 per cent. A small quantity of fluorspar added to the slag has a negligible effect upon the analysis.

The average analysis of the final slag taken from the open-hearth furnace on nineteen consecutive heats just before tapping is as follows: SiO_2 15.43 per cent., FeO 19.27 per cent., Al_2O_3 3.66 per cent., MnO 8.02 per cent., CaO 45.02 per cent., MgO 6.37 per cent., P_2O_5 1.80 per cent., S 0.031 per cent.

The average analysis of the steel prior to tapping these same heats was as follows: Carbon 0.23 per cent., manganese 0.26 per cent., silicon 0.010 per cent., phosphorus 0.007 per cent., sulfur 0.015 per cent., nickel 0.66 per cent., chromium 0.00 per cent. After it is tapped from the open-hearth furnace into a 75-ton ladle, the steel is teemed through a 2½ in. nozzle into two 40-ton basic electric furnaces for deoxidizing and finishing. Usually 2 lb. of 50-per cent. ferrosilicon and 3 oz. of aluminum for every ton of steel tapped from the open hearth are added to the ladle, to take up any oxygen present, which might lower the carbon content while the steel was in the ladle.

An average analysis of the slag left in the ladle from the nineteen heats, after teeming into the 40-ton furnace was as follows: SiO_2 17.27

per cent., FeO 18.32 per cent., Al_2O_3 5.75 per cent., MnO 7.84 per cent., CaO 42.79 per cent., MgO 8.15 per cent., P_2O_5 1.65 per cent., S 0.028 per cent.

The average analysis of the metal as teemed into the electric furnaces from the open hearth on the same heats was as follows: carbon 0.20 per cent., manganese 0.23 per cent., silicon 0.037 per cent., phosphorus, 0.007 per cent., sulfur 0.016 per cent., nickel 0.67 per cent., chromium 0.00 per cent. Both the furnace and the ladle slags show a slight increase in silica and alumina, which may be caused by the addition of the ferrosilicon and aluminum into the ladle. Some of these same elements may have been washed from the sides of the ladle and floated up into the slag. A comparison of the steel analysis will show that the silicon increased slightly; also, that there was a slight drop in carbon and manganese while the steel was in the ladle. The average phosphorus content of the charge into the open hearth was about 0.08 per cent., because of the comparatively low phosphorus in the crop ends.

After teeming the molten open-hearth steel into the 40-ton electric furnaces, a new slag is made up of burned lime, fluorspar, and ground coke. This represents, in weight, about 3 per cent. of the metal charged and is added from time to time, depending on the condition of the bath and the consistency of the slag. The operation from now on is a deoxidizing one. Under normal conditions, the bath is held from 3 to 5 hr. in a reducing atmosphere. The burned lime used in making up the new slag from the electric furnace showed the following analysis: SiO_2 2.50 per cent., $Fe_2O_3 + Al_2O_3$ 1.50 per cent., CaO 68 per cent., MgO 20 per cent.; loss on ignition 8 per cent. The MgO content is higher than usual, but a local lime is used for economic reasons; regular practice limits the MgO content to 5 per cent.

The final slag from the electric furnaces, after finishing the steel, showed the following approximate analysis on six consecutive heats:

SiO_2, Per Cent.	Fe, Per Cent.	Al_2O_3, Per Cent.	Mn, Per Cent.	CaO, Per Cent.	MgO, Per Cent.	P, Per Cent.	S, Per Cent.	CaC_2, Per Cent.
15.10	0.64	1.98	0.27	58.24	16.13	0.020	0.281	1.23
8.16	0.70	3.32	0.11	64.01	16.98	0.067	0.281	1.14
11.97	0.66	1.74	0.53	57.95	14.53	0.082	0.188	0.97
9.20	0.58	4.39	0.40	61.76	12.77	0.044	0.360	1.31
4.32	0.74	2.63	0.14	63.11	16.21	0.016	0.393	1.30
17.60	0.49	3.26	1.05	58.32	13.28	0.030	0.337	1.33

The high MgO in these slags comes from the high MgO in the lime used. The low sulfur is caused by the low sulfur in the charge. The high basicity of this slag and its freedom from metallic oxides, compared with the slag from the open-hearth furnace, should be noted. Unless the slag and steel are thoroughly deoxidized, it would be impossible to

form the carbide slag; without such a slag, it would be impossible to eliminate the sulfur from the steel.

The finished steel on these same six heats showed the following analysis:

Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Nickel, Per Cent.	Phosphorus, Per Cent	Sulfur, Per Cent.
0.32	0.71	0.250	0.36	0.022	0.009
0.36	0.74	0.241	3.03	0.013	0.008
0.29	0.74	0.238	2.78	0.010	0.007
0.35	0.71	0.200	0.31	0.013	0.008
0.38	0.67	0.210	2.97	0.010	0.008
0.30	0.78	0.215	2.83	0.013	0.010

The low sulfur in the final slag denotes the possibility of removing a greater amount from a steel of higher sulfur content from the open hearth. This would result from using a lower grade of scrap and pig iron with higher sulfur content in making up the charge for the open-hearth furnace. This might occur in plants where miscellaneous scrap is purchased in the open market and where crop ends are not so low in sulfur as those at this plant.

Description of Reactions

The reducing atmosphere and high temperature existing in the electric furnace permit the following reactions: When the molten steel comes from the open hearth, it contains oxides, principally in the form of FeO and MnO. As the MnO is less soluble in the molten metal than the FeO, it rises to the slag, which has been added on top of the steel as teemed into the electric furnace. This slag contains CaO and C. As the MnO rises to the slag, the following occurs:

$$MnO + C = Mn + CO \quad (1)$$

The Mn goes back to the bath and the CO is liberated as a gas. When the Mn goes back to the bath, the following reaction takes place:

$$FeO + Mn = Fe + MnO \quad (2)$$

Reaction (1) again takes place. When this reaction is complete and all metallic oxides eliminated from the slag, another reaction between the lime and carbon takes place, in which calcium carbide is formed:

$$CaO + 3C = CaC_2 + CO \quad (3)$$

This reaction, however, will not be stable as long as there is a migration of either MnO or FeO from the bath to the slag. In this case, the following occurs:

$$CaC_2 + 3MnO = CaO + 3Mn + 2CO \quad (4)$$

or

$$CaC_2 + 3FeO = CaO + 3Fe + 2CO \quad (5)$$

As long as the slag retains its carbide condition after repeated rabbling, it may be assumed that the bath has been freed from oxides. When reaction (3) becomes stable, it is possible to eliminate the sulfur from the steel.

The sulfur is present as FeS and MnS. As calcium has a greater affinity for sulfur than either Fe or Mn, its presence in the slag causes the following reaction:

$$3FeS + CaC_2 + 2CaO = 3Fe + 3CaS + 2CO \quad (6)$$

and

$$3MnS + CaC_2 + 2CaO = 3Mn + 3CaS + 2CO \quad (7)$$

The Fe and Mn return to the bath, the CO goes off as a gas, while the CaS is held in the slag. If for any reason the slag should take up any metallic oxide, the conditions expressed in equations (6) and (7) would be reversed and the calcium would give up the sulfur as follows:

$$CaS + FeO = FeS + CaO \quad (8)$$

or

$$CaS + MnO = MnS + CaO \quad (9)$$

A simple test for the presence of CaC_2 in the slag may be made by sprinkling water on the slag, when acetylene gas will be given off as a result of the following reaction:

$$CaC_2 + H_2O = CaO + C_2H_2$$

Conclusions

The manufacture of ordnance forgings from electric steel is not an innovation. It was tried, during the war, in a number of plants. Some of these plants were not so successful as others, probably because the managers were not sufficiently experienced in the many other phases of manufacture necessary in the making of ordnance forgings.

Steel made in an electric furnace will not be of the best quality unless all operations and reactions are preformed completely and satisfactorily. Electric steel with its greater freedom from oxides and non-metallic impurities is more uniform, more homogeneous, and more dense than ordinary open-hearth steel, and if it is cast at too high a temperature or chilled beyond a certian point in the mold, incipient cracks will develop. These minute cracks are radial and are most frequently found near the center of the ingot or forging. Numerous electric-steel plants working on ordnance material, during the war, were troubled with these defects, which from their physical appearance in test bars were called "snow flakes."

A diversity of opinion has always existed between the leading ordnance steel plants regarding the method of teeming steel into the molds.

Some have consistently adhered to bottom pouring while others have claimed better results from top pouring direct, or through funnels or boxes. The method apparently makes little difference if the steel is placed in the mold at the proper temperature and has been properly cleansed before teeming. Top pouring direct obviates the danger of getting runner brick into the ingot, which frequently occurs in the case of bottom pouring. It also obviates the danger of sand washing into the molds with the metal from the funnel or box. Bottom pouring will give a better surface on the ingot and for some purposes may be more desirable.

DISCUSSION

HARRY T. MORRIS,* Bethlehem, Pa.—Was this armor plate forged in both directions? Has the author experimented frequently with transverse and longitudinal bars from armor plate in which the forging was done in both directions? Has he found that irrespective of the content of sulfur, up to 0.06 per cent., the forging in both directions, for a time in one direction and for another time at right angles, produces reasonably consistent and comparable results in the tensile bars, both transverse and longitudinal?

WILLIAM J. PRIESTLEY.—An examination of the photomicrographs of the armor plate made of electric steel will show that the inclusions are approximately the same magnitude in the bars taken in both directions, and that they are smaller than the enclosures in the other armor plate. It would be expected that when the plate was forged in two directions, the inclusions would be drawn out in both directions and they would be more apparent than in the case of the longitudinal bar taken from the plate forged only in one direction.

Figs. 4 and 5 are photomicrographs taken from transverse and longitudinal test bars from a heat-treated armor plate of foreign manufacture, which showed very poor results in ballistic tests. Fig. 4 was taken parallel to the direction of forging the ingot and shows the non-metallic enclosures in the steel elongated. The physical properties of this bar, taken at right angles to the direction of forging, showed the following characteristics: Tensile strength 111,000 lb. per sq. in.; elastic limit, 55,000 lb. per sq. in.; elongation, 13.4 per cent.; contraction, 23.9 per cent.

Fig. 5 was from a longitudinal test bar taken parallel to the direction of forging the ingot; it will be noted that the impurities are round and are cross-sections of the enclosures as shown in Fig. 4. The results of the physical tests on this bar were as follows: Tensile strength, 100,000 lb. per sq. in.; elastic limit, 68,000 lb. per sq. in.; elongation, 26.5 per cent.; contraction, 65.5 per cent.

* Metallurgical Engineer, Bethlehem Steel Co.

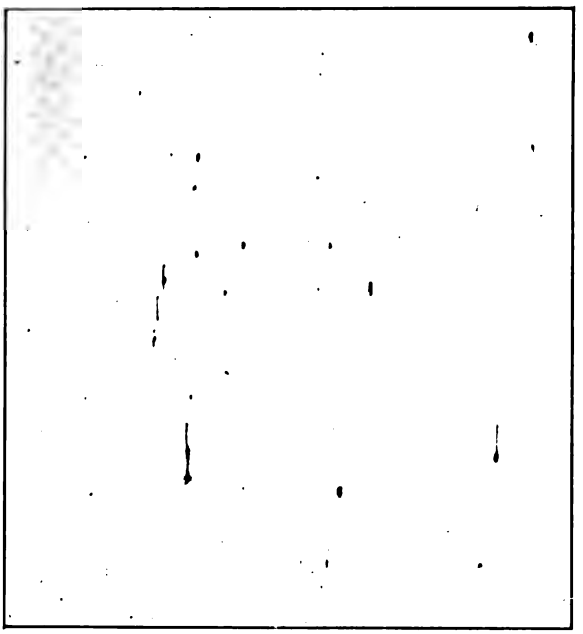


FIG. 4.—TRANSVERSE TEST BAR FROM HEAT-TREATED ARMOR PLATE OF FOREIGN MANUFACTURE. × 25.

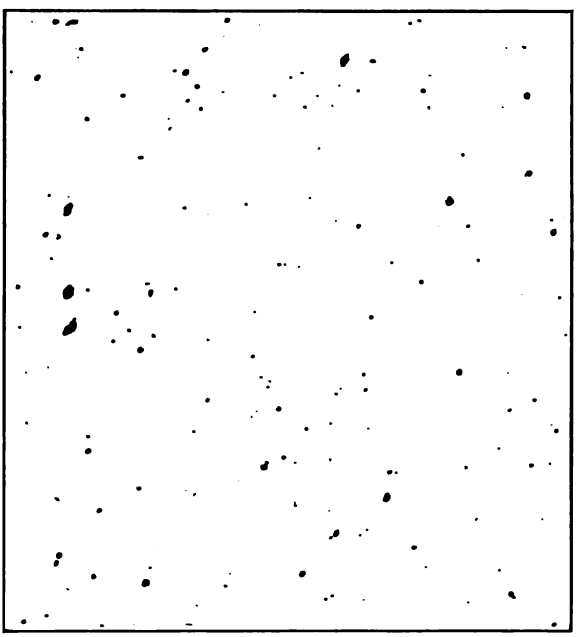


FIG. 5.—LONGITUDINAL TEST BAR FROM FOREIGN HEAT-TREATED ARMOR PLATE. × 25.

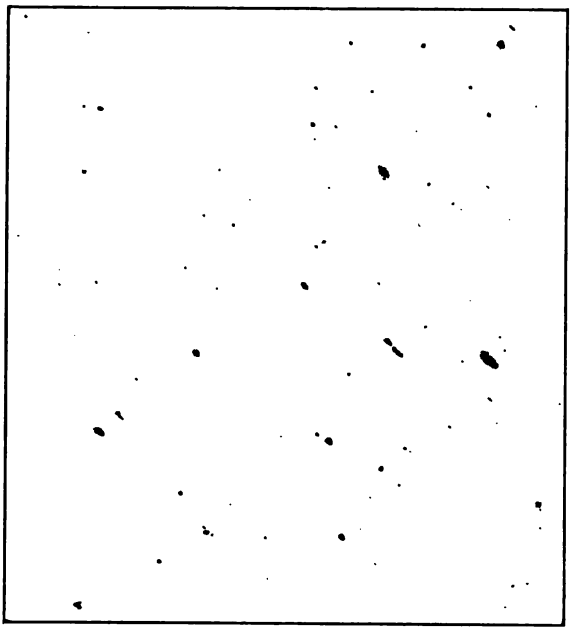


FIG. 6.—TRANSVERSE TEST BAR FROM GREEN ANNEALED ELECTRIC STEEL ARMOR PLATE. × 25.

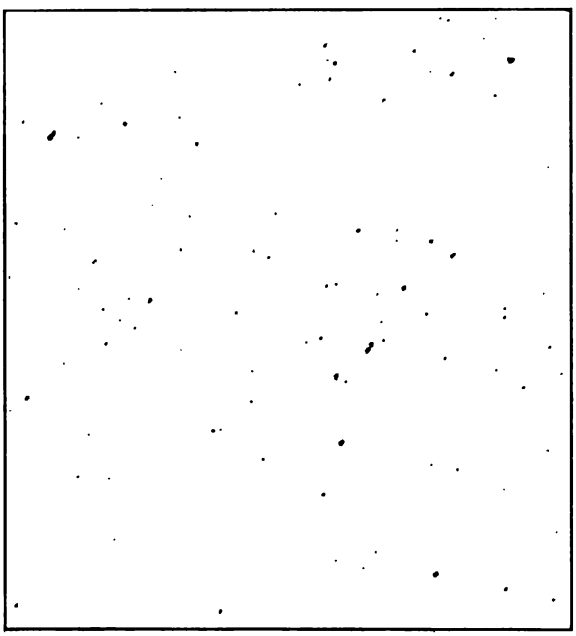


FIG. 7.—LONGITUDINAL TEST BAR FROM GREEN ANNEALED ELECTRIC STEEL ARMOR PLATE. × 25.

Figs. 6 and 7 are from transverse and longitudinal test bars taken from an armor plate made of electric steel from which the oxides and non-metallic enclosures have been removed. The results of physical tests on the transverse test bar were: Tensile strength 101,500 lb. per sq. in.; elastic limit, 61,000 lb. per sq. in.; elongation, 26.5 per cent.; contraction, 65.8 per cent. The longitudinal test bar, Fig. 7, was taken from the same plate as the transverse bar and showed the following physical properties: Tensile strength, 104,000 lb. per sq. in.; elastic limit, 57,000 lb. per sq. in.; elongation, 25.3 per cent.; contraction, 63.5 per cent.

The forgings from which the bars shown in Figs. 6 and 7 were taken were only green annealed, whereas the plates from which the other bars were taken were heat treated. It will be noted that the electric steel, which is free from non-metallic inclusions, has practically the same strength and ductility in two directions, whereas the steel shown in Figs. 4 and 5, which contains a greater amount of non-metallic inclusions, has strength and ductility only in one direction and is very weak and lacks toughness and ductility in the other direction.

C. P. PERIN, New York, N. Y.—I did not understand that was the question; I thought Mr. Morris asked as to the deleterious effect of sulfur, although the steel were forged in both directions, whether it would have a bad effect.

HARRY T. MORRIS.—I asked about the physical results, not the photomicrographs. It is not to be disputed that if the sulfur content is three times as high in one piece of steel as in another, the microscope might show more inclusions in a given area where the sulfur is high; but the thing that I wanted to show was that it does not necessarily follow that specimens from a piece of steel containing 0.04 per cent. or more sulfur will not give practically equal physical properties in both directions; that is, there is some treatment besides the elimination of sulfur that will give it equal physical properties in both directions.

W. J. PRIESTLEY.—We have tried to heat-treat foreign inclusions out of steel. Some melting men say that it can be forged out and some say that it can be heat-treated out, but I have never seen it done, nor have I seen it broken up or scattered.

HARRY T. MORRIS.—The question of sulfur in proportions up to 0.04, 0.05, 0.06 per cent. is an important one in all kinds of steel, and there are differences of opinion among engineers, producers, and open-hearth men as to the effect of sulfur up to 0.05 or 0.06 per cent. Some engineers, open-hearth, and electric-furnace people, and steel producers will not admit that a steel with 0.06 per cent. sulfur is not necessarily an inferior steel.

This paper seemed to indicate that if an armor plate, for instance,

had 0.05 or 0.06 per cent. sulfur (such sulfur is not shown in this paper but the inference might be drawn by those not familiar with this subject) it would not be quite as good as one with 0.03 per cent. sulfur. I do not believe that the actual resistance in a firing test (where projectiles are fired against armor plate) will demonstrate that a 0.06 per cent. sulfur armor plate is necessarily poorer than one with a 0.03 per cent. sulfur content.

JAMES H. GRAY,* New York, N. Y.—When I first read this paper, I thought the author had found a decided difference in the quality of the steel, getting transverse tests practically equal to longitudinal tests in gun steel forged in only one direction. It seemed as if there was a difference between 0.025 per cent. sulfur in certain electric steels and under 0.01 per cent. in the author's steel. The author seems to prefer low sulfur because it is an indication that he has properly made the steel in the electric furnace; that is, he could not desulfurize the steel without having previously cleaned and deoxidized it. If he could express that idea, it would perhaps clear up the difficulty as to the real value of lower sulfur.

W. J. PRIESTLEY.—In order to reduce sulfur from steel down as low as 0.008 or 0.006 per cent., the steel must be thoroughly deoxidized. A carbide slag is necessary, to take out the last traces of sulfur. I do not want to convey the idea that it is the sulfur that is doing the harm, but if the sulfur can be brought down that low, you must get all the oxides out of the steel.

W. P. BARBA, Philadelphia, Pa.—The author is discussing the manufacture of this product in an electric furnace only. Mr. Morris questions the initial and final content of sulfur, irrespective of the process used to melt and produce the ingot. You have, therefore, two different premises, which cannot be compared without qualification.

There is in armor plate a third dimension, that is from face to face through the plate; if, in my works practice, I saw such a test bar with a cup fracture, I would cut a whole section through the plate and study that macrostructure in order to find out whether or not it had the necessary resistance properties. Because of the successive laminations, exactly like the successive pages of a book, were a projectile fired against the plate, it would meet sheet after sheet of resisting metal, the values of which are not exhibited by a pulled bar. The pulled bar was used to determine if the works superintendent had gotten his grain-size into the most satisfactory condition to resist the impact of a shell at the proving grounds; but he does not want to see a cup fracture in all three dimensions on his plate, therefore, I do not give too much value to cup fractures. As Mr. Morris pointed out, the plate could have been forged in two directions,

* Metallurgical Engineer, U. S. Steel Corpn.

while in the slab or ingot form, and by forging thus you can get practically equal test bars. There is an entirely different set of conditions in the plate to observe from face to face; yet, the plate showing in that third dimension test bar 1 per cent. stretch might keep out a shot.

W. J. PRIESTLEY.—The first two plates made of electric steel had the laminated structure, with fissures between, about which Colonel Barba has spoken. We thought that if we could not improve on that, we were not going to improve our armor plate. We wanted a plate that was homogeneous in structure with a perfect continuity of metal through the thickness, exactly as in the other dimensions. That was obtained from clean steel free from oxides by preventing the ingot from cooling in the mold and by preventing the plate from cooling down after forging. The steel was kept hot all the way through and eliminated that structure. Unfortunately, we did not have time to get a tensile-test bar out of the third dimension, but from physical appearances the structure was homogeneous and lacked that woody formation with fissures generally found in armor plate made in the basic open-hearth furnace. The last plate I saw tested ballistically did not have these fissures; the back of the plate opened up like an orange peel. This plate was rated high. On plates with this laminated structure I have seen a perfect disk pushed from the back in firing tests. It has been my experience that a plate that will open up in the back like an orange peel and hold together on the perimeter of the impact is stronger and better than a plate that will fail by a straight, flat button going out of the back of the plate.

HAAKON STYRI,* Philadelphia, Pa.—I have never obtained any satisfactory explanation as to why some ingot molds are made corrugated with sharp corners and others with round corners, or some with six corrugations, some with eight, and some with more. Some plants get good results with sharp-cornered molds and others get better results with round corners.

In Howe and Barba's paper, an analogy was drawn with cylindrical and corrugated drain pipes, the latter not bursting when the water would freeze. But water expands on freezing and steel contracts. To resist liquid pressure the cylindrical form would be stronger than the corrugated. Is not the explanation of various successes with different ingot molds rather the adaptation of such molds that will best suit the pouring practice at the particular plant or some variation of the practice to fit the mold, so that the resulting skin of the ingot will be strong enough and not burst.

W. P. BARBA.—Doctor Howe's philosophy on the reported practice, supported by sketches, blueprints and experience dating back to 1897,

* Chief of S. K. F. Laboratory.

will answer the questions just raised. The practical point is that about ten factors of design and of practice are brought into consideration.

FRANK D. CARNEY, New York, N. Y.—With the octagon sharp-cornered mold, Fig. 8, when the dentritic or columnar crystals start to grow in from the concave sides they produce a plane of weakness at each corner, trapping the impurities, and it requires great skill in pouring and temperature control to prevent a plane of weakness at the corners.

Our experience at the Bethlehem Steel Co. was similar to Mr. Priestley's. Sharp-cornered octagon ingots sometimes gave poor transverse tests if test specimens crossed at this point. If the octagon mold was designed with round corners, we did not have the trapping effect in the corners. This type of mold is fool-proof as it allows a wider margin in rate of pour and pouring temperatures. This ingot could be rolled with good results on a blooming mill.

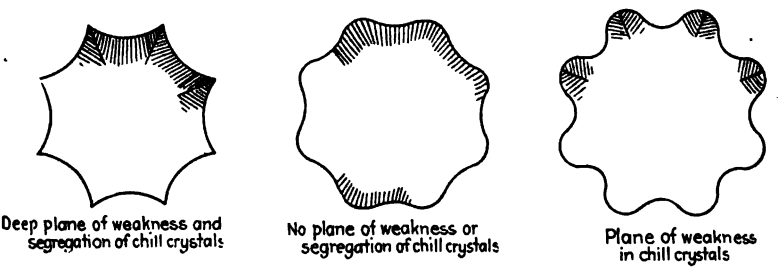


FIG. 8.

For heavy ordinance work our practice was to slice the ingots in a lathe, bore out the center and inspect the end surfaces, from time to time, with sulfur prints. We never found planes of weakness in the round-cornered ingots and therefore abandoned the use of sharp-cornered molds.

W. P. BARBA.—Mr Carney has correctly shown the two extremes that lie in those two forms of ingot molds. I was, to some degree, familiar with the experience of the Bethlehem Steel Co., and have noted exactly the same thing. If the correct relation is had between cross-sectional areas, the radius to what we call the flat and the radius to what we call the corner, none of the troubles that Mr. Carney mentions, will be experienced. It is a phase through which one must feel his way, and when the right method is found the wrong one should be abandoned.

W. L. HARBRECHT,* Niagara Falls, N. Y.—The author says that he saw flakes only in electric steel; I have seen them in both the acid open-hearth and electric steel, and more frequently in the latter. By electric steel I mean that made by the triplex process.

* Metallographist, Electro-Metallurgical Co.

W. J. PRIESTLEY.—I have seen so-called flakes in acid and basic steel. I have examined the defects closely and have found that in the center of the flake, in the acid or basic open-hearth steel, there would be a slag inclusion as a rule; but my experience has been that with the typical electric steel flake there is no foreign inclusion.

W. L. HARBRECHT.—We have examined flakes from both kinds of metal and we did not find any inclusion in either, except that at the edge of the flake, by making a macroetch, we sometimes would see a small dotted line of inclusions along the outside of the flake.

C. P. PERIN.—Was that characteristic of the electric or of the open-hearth steel?

W. L. HARBRECHT.—Of both. When examined with a microscope, we did not see any difference in structure or in any other way.

GEORGE F. COMSTOCK,* Niagara Falls, N. Y. (written discussion).—This paper is of great interest, showing as it does the detrimental effects of sulfides and other non-metallic inclusions on the quality of steel. It might be suggested, however, that segregation has an important influence on the degree of harm occasioned by a given amount of non-metallic matter included, because the arrangement of a number of particles in groups or streaks, as is suggested by the photomicrographs in Fig. 1 and Fig. 3, undoubtedly gives a much more serious effect than would a uniform distribution of the same amount of material. Probably one reason for the success attained at the Naval Ordnance Plant in making this steel was the care and time available for insuring a complete absence of segregation, such a condition being practicable at this plant on account of the lack of necessity for a large tonnage of output in a given time.

It does not seem correct to state that oxides are "eliminated by the addition of deoxidizers, such as ferromanganese, ferrosilicon, aluminum, etc." Oxygen and iron oxide are doubtless eliminated by these reagents, but at the cost of producing other oxides in the steel, the net result being a formation of oxides rather than their destruction. The oxide of aluminum, especially, is difficult to eliminate from steel in which it has once been formed, and it is nearly always possible to identify steel in which it has been used, by a microscopic search for alumina particles in a polished section. The deoxidizer least liable to contaminate steel with its oxidation products is ferro carbon-titanium, which is not mentioned. Titanium oxide has been found to render slags and oxidation products of other deoxidizers more fusible, and the carbon in this alloy assists in the production of a lively reaction in the steel, which is entirely

* Titanium Alloy Mfg. Co.

completed in the ladle in a very reasonable time. No noticeable contamination of the steel by oxides is evident in steel properly treated with this alloy, and an exhaustive series of tests in rail steel has furnished unquestioned proof of its effectiveness as a preventive of serious segregation. It is unfortunate that this method of treating basic open-hearth steel has not been given a thorough trial in the manufacture of ordnance material, for the lack of success from such steel might be overcome, in this way, at much less expense than by the method of duplexing with an electric furnace.

E. J. JANITZKY,* South Chicago, Ill. (written discussion).—The author states that usually 2 lb. of 50-per cent. ferrosilicon and 3 oz. of aluminum are added to the ladle for every ton of steel tapped from the open-hearth, to take up any oxygen present, which might lower the carbon content while the steel was in the ladle. These additions appear unexcelled as deoxidizers as no gases are developed in their reactions but as they hinder the expulsion of occluded gases from the metal, their use is questionable.

The products of oxidation of silicon and aluminum have ample time during the refining period to enter the slag, which is no reason for discriminating against their use. Ferrosilicon and aluminum will kill the steel, in other words, eliminate the liveliness of the steel bath, hence they will not allow a gradual natural dead melt.

A ferromanganese addition will counterbalance supposed carbon loss. Manganese is one of the main deoxidizing elements in the electric-furnace process and the loss of metallic manganese in the ladle would in all probability counterbalance the certain loss of aluminum and silicon, neither of which has any influence on the physical properties of the steel nor takes part in the deoxidizing reactions, as does manganese. Otherwise a higher initial carbon content of the open-hearth melt or the addition of some anthracite to the ladle would be a less expensive way and would also offset the carbon loss. Either anthracite or ferromanganese will take part in the deoxidizing reaction, but when pouring into the electric furnace, the opportunity of gas expulsion is given, whereas silicon and aluminum would hinder it. As degasification cannot be performed with the addition of ferro-alloys, the refining of the bath must take care of it. The degree to which it takes place is a matter of speculation.

The influence of occluded gases on the physical properties of steel has not been thoroughly studied. Recent experiments, however, seem to show that their influence is greater than we assume. Mars and others have pointed to the improved quality that can be obtained by cooling the bath below the pouring temperature and then reheating it to the required temperature. By repeating this procedure, the minimum gas

* Metallurgist, Illinois Steel Co.

content can be obtained. The electric furnace facilitates degasifying in this manner. That occluded gases which are partly liberated in solidification, as well as non-metallic inclusions and segregation, are responsible for weakening the transverse structure is not yet perfectly established, but recent experiments seem to indicate this fact; therefore degasification is beneficial to the transverse properties of the steel and its importance should not be overlooked.

Effect of Quality of Steel on Case-carburizing Results

By H. W. McQuaid,* M. E., and E. W. Ehn.* M. E., Canton, Ohio

(New York Meeting, February, 1922)

It is usually assumed that chemical specifications are sufficient for steel to be used for case carburizing, and if the steel analyzes within the ordinary limits specified for steel for this purpose, no difficulty traceable to the steel used should be encountered in obtaining satisfactory results in the case carburizing and hardening. Much work has been done to determine the effect of various alloying elements on the rate of carbon penetration, etc. but, to our knowledge, little if anything has been published in regard to the effect of the quality of the steel on the final results in the hardening of case-carburized steel parts.

The writers believe that the structure of the case both before and after quenching is greatly affected by the actual condition of the steel itself as made, and that for good results in the case-carburizing and hardening departments, the steel should be of the best possible quality as regards non-metallic impurities.

It is the purpose of this paper to prove that the presence of excess dissolved oxides in the steel, as made in the melting furnace, affects permanently the results obtained in carburizing and hardening and that it is possible that the presence of dissolved oxide can result in total unfitness of low-carbon steel for case hardening purposes.

When races and rolls for roller bearings are made from a low-carbon steel, case carburized and hardened, it is of primary importance that the results of this treatment be of the highest quality. It is necessary, therefore, that in the case-carburizing work each detail be rigorously checked to avoid any defects which would cause the loss of much time and material.

The case carburizing with which this paper deals was done in underfired oil furnaces. The temperature of each furnace is controlled by means of a platinum platinum-rhodium thermocouple, in connection with a potentiometer indicator and potentiometer recorder. The temperature of each furnace is registered every 15 min. by an operator, who is continually checked by the automatic recorders.

* Metallurgist, Timken Roller Bearing Co.

The work prepared for carburizing is packed carefully in nickel-chrome carburizing pots of rather large size, 14 by 18 by 14 in. (36 by 46 by 36 cm.). When loaded, one of these pots will weigh approximately 500 lb. (227 kg.). Six of these pots constitute a furnace charge, making a total of 3000 lb. per charge. The time required to bring this charge to the carburizing temperature (1700° F.) varies from 9 to 10 hr., depending on the size of the pieces being carburized.

In bringing a large carburizing pot to the required temperature, the temperature of the corners and the material near the surface is always considerably ahead of that of the material deeper in the pot, hence carburizing starts at these points. With charcoal-barium carbonate compounds, which are more active at lower temperatures and produce a case in a much shorter time than bone-base compounds, the effect of this difference in temperature of different parts of the same pot is to cause a corresponding variation in case depth and carbon content. With the bone-base compounds, the time required to bring the charge to heat is only a small percentage of the total time required for carburizing as compared to that required with the charcoal-barium carbonate compounds. With the bone-base compounds the time during which the corners of the pot will be at carburizing temperature will only be from 10 to 15 per cent. longer than the time during which the work in the center of the pot is carburizing. With the charcoal-barium carbonate compounds, the corresponding difference will be from 30 to 40 per cent. It has, therefore, been considered advisable in the carburizing of roll-bearing parts, where the case obtained is a direct factor in the life of the bearings, to carburize with bone-base compounds, the extra time required being compensated by the assurance of uniformity in the results obtained.

With each pot of work are packed pieces for check tests. These pieces when cold are taken from the pot, reheated to 1420° to 1440° F., quenched in water, broken, and the fracture examined. A 15-per cent. solution of nitric acid is used to develop the depth of case.

In spite, however, of the most careful inspection, trouble would occasionally develop in the hardening of case-carburized material, and large quantities of material would be rejected after hardening because soft spots were found by the file. This, it was noted, occurred in particular lots of work when nearly 100 per cent. of the pieces showed soft spots in the hard inspection test. The pieces, it was also noted, could be traced almost exclusively to certain heats of steel made in basic open-hearth furnaces.

It was assumed, as has long been the custom, that all steel within the chemical specifications would react the same in the carburizing process, hence all efforts to locate the cause of soft work were directed to the quenching, heating, or carburizing compound, or in some preliminary treatment, such as forging or rolling.

The carburized work, in the form of cups and cones for Timken bearings, is quenched in special fixtures designed to produce the quickest possible chilling of the pieces—clear, clean water at 65° to 70° F. being forced against the surface of the raceway under a pressure of 50 lb. per sq. in. The pieces are heated in especially designed oil- or gas-fired furnaces of the rotating-table type, the pieces being automatically carried through the heated zone to the outlet door, from which they are taken by the operator and quickly placed in the mechanically operated quenching apparatus. The process is so arranged that there is the minimum possibility of variation in the temperature of the pieces as they enter the quench. When it is found that a certain batch of work will not harden properly, special care is taken to insure proper quenching and work from batches known to be satisfactory is mixed, as a check, with the work giving trouble. If under these conditions the work from good batches hardens properly whereas the other work will not harden, it is accepted as proof that the cause of the soft work antedates the hardening operation. Great care is taken to check this conclusion. If when trouble of this character occurred the hardening temperature was raised considerably above the normal operating range (1420° to 1440° F.), little if any improvement would be found; although it was observed that the high temperature generally had little effect on the grain of the case, the usual coarseness of fractured case not being obtained with increased temperature.

When it was found that large quantities of certain sizes would not harden properly, the first step taken was to recarburize for a short time. This, in nearly every instance, failed to improve the result of the hardening. When it was found that the work that resisted all attempts to harden was confined to certain lots of basic open-hearth steel, checks were instituted to determine the cause of the difficulty.

When work from these lots of basic open-hearth steel was packed together (*i.e.* within ½ in.) in the same carburizing pot with the best grade of electric-furnace steel and it was found that the electric-furnace product gave excellent results in hardening, producing a deep martensite, whereas the open-hearth steel products resisted all attempts to harden and the case was of variable martensite with a deep and variable troostitic zone, it was assumed that the cause of the difficulty must lie in some previous stage of manufacture and the carburizing department was eliminated as a factor. At this time representative compounds of the various types of carburizing agents were tried; charcoal-barium carbonate, charred leather, and petroleum coke with added energizers all failed to improve results.

Samples were taken from forgings of basic open-hearth steel from the same shipments as those giving trouble and from electric-furnace steel and packed closely together in the same pot. It was found that the open-hearth steel results were very unsatisfactory while the electric steel

results were excellent. This check was then made on billets for the forging machines, bars from the rolling mills, blooms for the bar mill, and finally from the ingot. In all these cases the electric steel used gave satisfactory results while the basic open-hearth steel produced very poor results, the hardened work being soft in spots and the fracture of poor appearance. After a number of such tests were made, it became evident that the cause of the hardening department troubles could not be in the working of the steel before carburizing, in the carburizing department, or in the hardening department. All test results were carefully checked by microscopic examination.

Microscopic examination of many specimens of carburized work developed a striking difference between steels that would show soft areas after quenching and those that would be satisfactory. By a careful comparison of carburized steel from bars known to produce poor results with steel that gave good results, it became possible to determine, after carburizing, whether or not the pieces would have soft areas after quenching. It also became evident that, for some reason, a characteristic structure in the hypereutectoid zone was formed after carburizing in the steel giving trouble, which made it almost impossible to retain the normal martensite after quenching.

Microscopically, it became a simple matter to detect steel after carburizing that would not form normal martensite after the quenching, the difference between it and the normal steels being easily distinguished by the experienced observer (Figs. 1 and 2). Fig. 3 represents the hypereutectoid zone of a normal steel after case carburizing and slow cooling. The pearlite is very finely lamellar and the cementite exists as well-defined lines of fine but continuous formation at the crystal boundaries. Fig. 4 represents the hypereutectoid zone of an abnormal steel. This steel was carburized under exactly the same conditions as that of Fig. 3, both specimens being packed close together in the same carburizing pot. In Fig. 4, the pearlite of the hypereutectoid zone has partly broken down to form massive cementite and free ferrite; the cementite can be distinguished as ridges having a white background of ferrite. Fig. 5 shows the same specimen as Fig. 4 after etching with hot sodium-picrate solution. Steel that, after carburizing, gives the results shown in Fig. 3, we have here designated as normal; steel that under the same conditions produces the results shown in Fig. 4, we have designated as abnormal. Fig. 6 represents the gradation zone of normal steel, exhibiting the coarse crystal structure caused by the long exposure to the carburizing temperature (24 hr. at 1700° F.)

Figs. 7, 8, and 9 represent gradation zones of specimens of abnormal steel. The small crystal formation and the irregularity of this zone are characteristic of abnormal steel. There is also evidence that the structure of the core of a normal steel after carburizing is entirely different

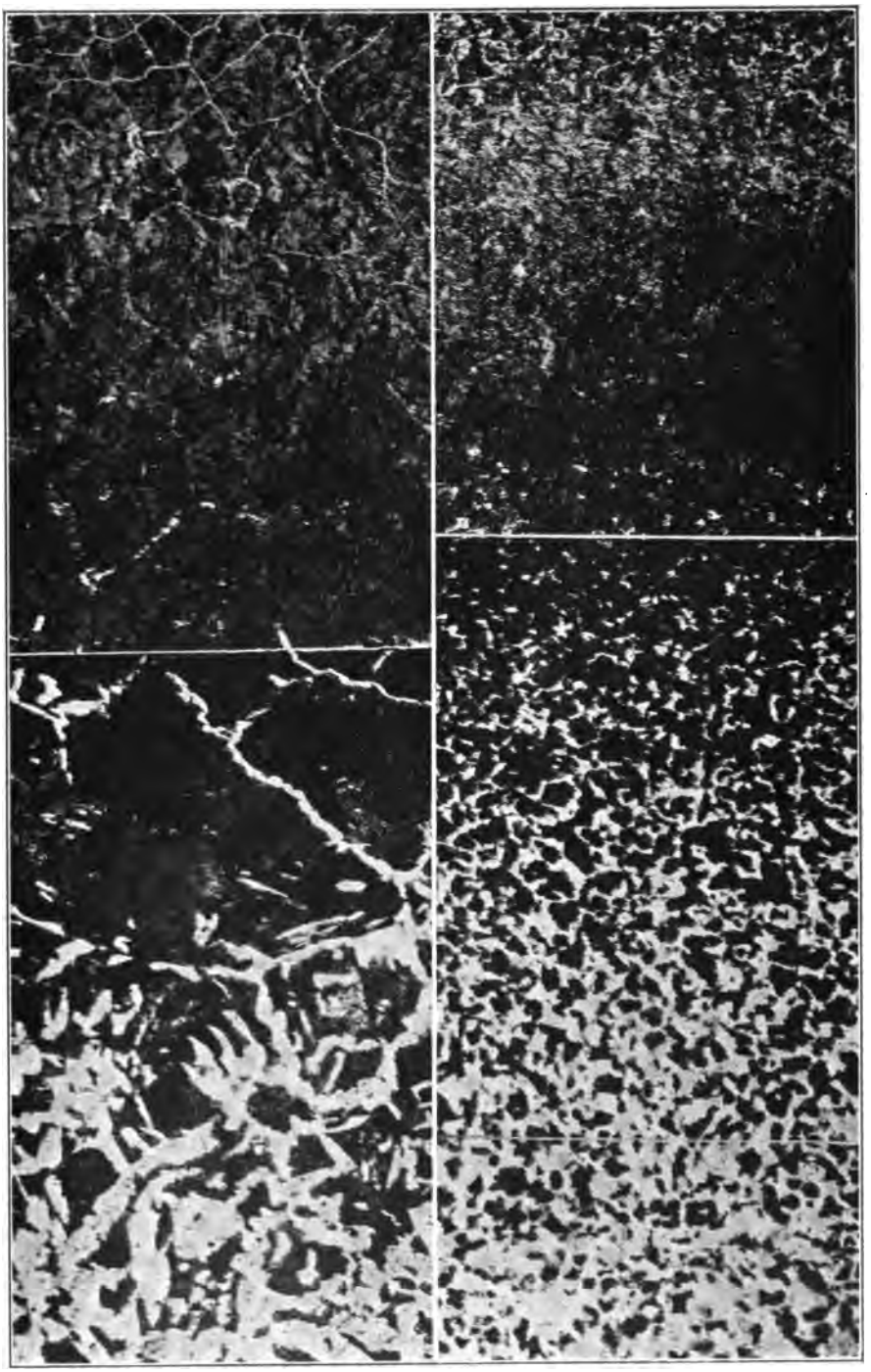


FIG. 1.—CASE OF NORMAL STEEL; 5 PER CENT. PICRIC-ACID ETCH. × 100.

FIG. 2.—CASE OF ABNORMAL STEEL; SPECIMEN PACKED WITH STEEL SHOWN IN FIG. 1. × 100.

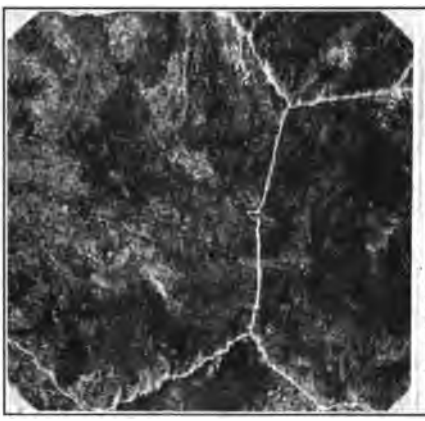


FIG. 3.—SECTION OF HYPEREUTECTOID ZONE IN NORMAL STEEL, FINELY LAMELLAR PEARLITE; NOTE MANGANESE-SULFIDE INCLUSION THROUGH CEMENTITE BOUNDARY OF TWO LARGE CRYSTALS. ETCHED WITH 5 PER CENT. PICRIC ACID. × 200.

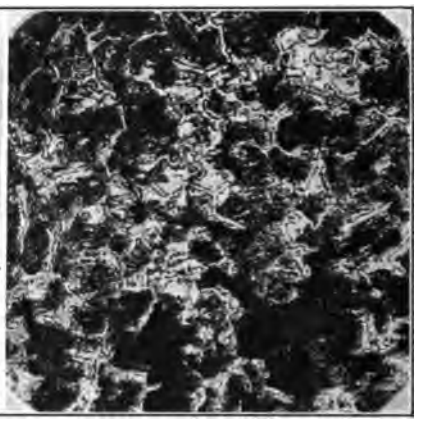


FIG. 4.—SECTION OF HYPEREUTECTOID ZONE IN ABNORMAL STEEL; NOTE RIDGES OF HEAVY CEMENTITE IN MASSES OF FERRITE. ETCHED WITH 5 PER CENT. PICRIC ACID. × 200.

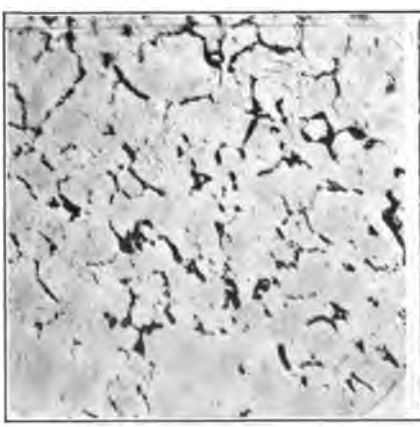


FIG. 5.—SECTION OF HYPEREUTECTOID ZONE IN ABNORMAL STEEL, SAME AS SHOWN IN FIG. 4, USING SODIUM-PICRATE ETCH. × 200.

FIG. 6.—GRADING ZONE IN NORMAL STEEL; NOTE LARGE GRAIN SIZE. ETCHED WITH 5 PER CENT. PICRIC ACID AND ALCOHOL. × 100.

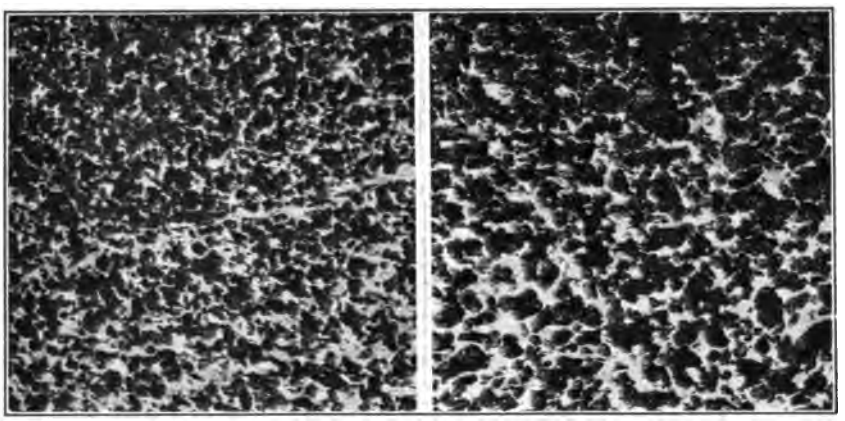


FIG. 7.—GRADATION ZONE IN ABNORMAL STEEL; NOTE SMALL GRAINS AND INDICATIONS OF BANDING TYPICAL OF THIS STEEL. ETCHED WITH 5 PER CENT. PICRIC ACID AND ALCOHOL. × 100.

FIG. 8.—SAME AS FIG. 7, BUT DIFFERENT STEEL.

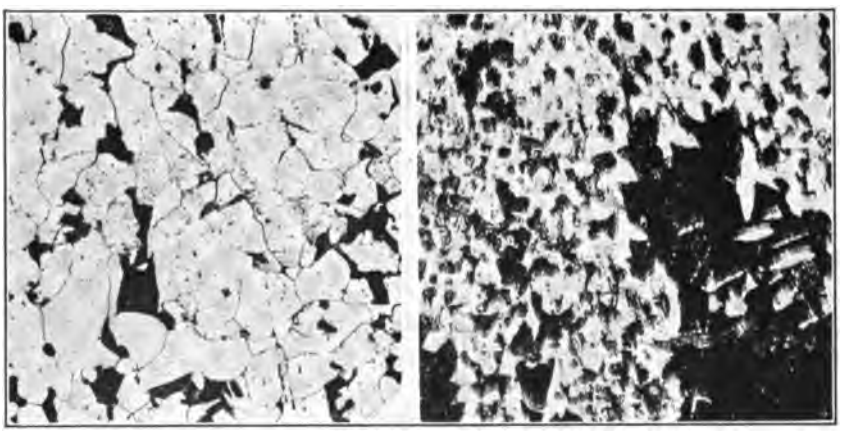


FIG. 9.—GRADATION ZONE OF MIXED NORMAL AND ABNORMAL STEEL. ETCHED WITH 5 PER CENT. PICRIC ACID AND ALCOHOL.

FIG. 10.—CORE OF CARBURIZED NORMAL STEEL. × 100.

than the structure of the core of the abnormal steel. In the core of a steel that produces a normal hypereutectoid case, the pearlite areas after carburizing are large, evenly distributed, and inclined to be angular in outline

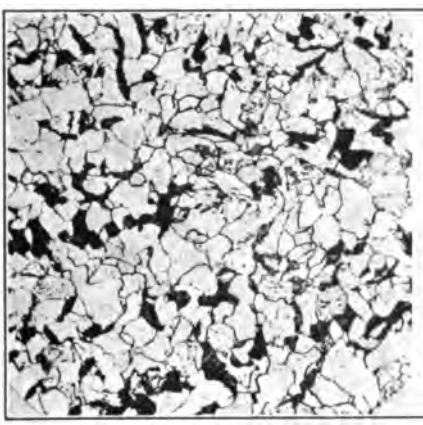


FIG. 11.—CORE OF CARBURIZED ABNORMAL STEEL. × 100.

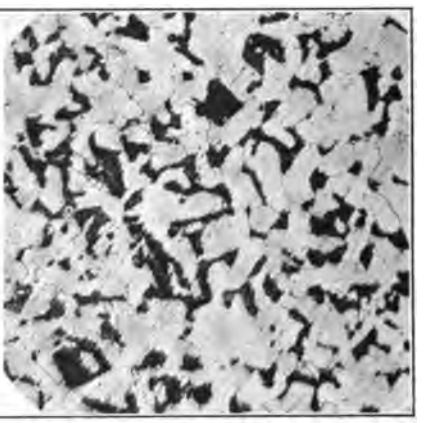


FIG. 12.—CORE OF NORMAL STEEL BEFORE CARBURIZING. × 100.

with sharply defined corners; whereas in steel in which the pearlite of the hypereutectoid zone is broken down after carburizing, the pearlite areas are small, more numerous, and not clearly defined, while banding and

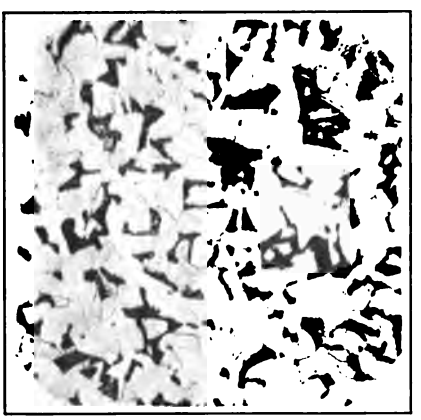


FIG. 13.—CORE OF ABNORMAL STEEL BEFORE CARBURIZING. × 100.

ghost lines are common. This difference is very characteristic and clearly evident, see Figs. 10 to 13. Figs. 14 to 19, represent the hypereutectoid zones of various samples of normal and abnormal steel. A little study will soon make clear the microscopic distinction, between the cases of normal and abnormal steel. Knowing that the breaking down of the

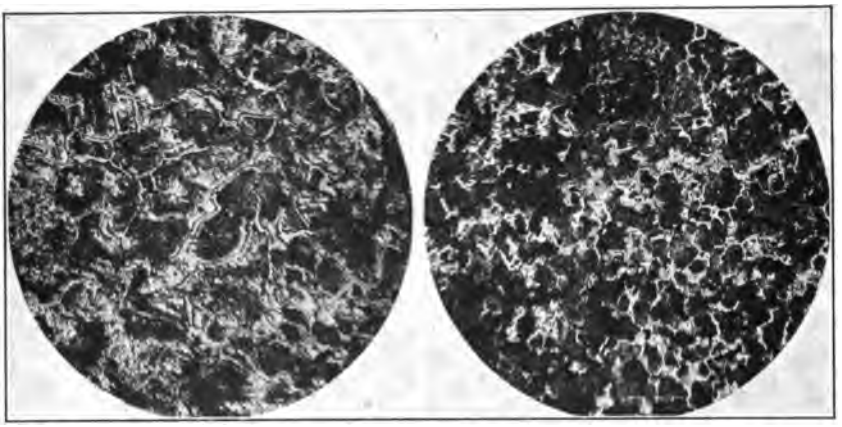


FIG. 14.—HYPEREUTECTOID ZONE, VERY ABNORMAL STEEL. × 100.

FIG. 15.—HYPEREUTECTOID ZONE, ABNORMAL STEEL. × 100.

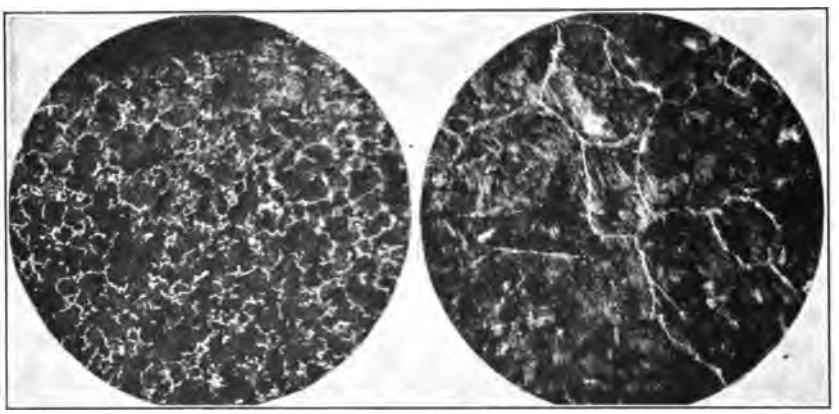


FIG. 16.—HYPEREUTECTOID ZONE, ABNORMAL STEEL. × 100.

FIG. 17.—HYPEREUTECTOID ZONE, NORMAL STEEL. × 100.

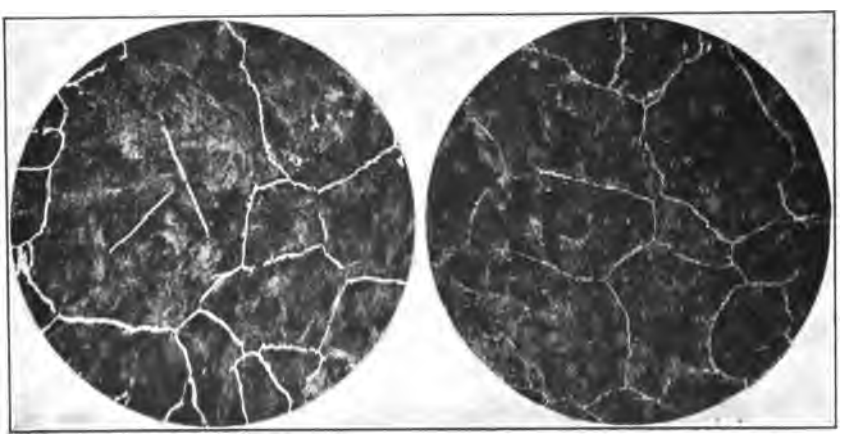


FIG. 18.—HYPEREUTECTOID ZONE, NORMAL STEEL. × 100.

FIG. 19.—HYPEREUTECTOID ZONE, NORMAL STEEL. × 100.

normal pearlite structure of the hypereutectoid zone was followed by soft spots after quenching, it became necessary to determine where the cause of this abnormal steel lay and to devise means for its elimination.

As stated, samples at various stages of conversion, from the ingot to the machined forging, were taken to determine, if possible, whether or not the cause of the unstable pearlite after carburizing did not lie in some step of the process of converting the ingot into the part ready for carburizing. It was found in most cases that the same condition existed at all stages of conversion and that with the steels used as a check the carburizing results were apparently unaffected by the condition of the steel, *i.e.*, whether cast, rolled, or forged. After many tests covering a considerable time, it was decided that the cause of the unstable pearlite of the hypereutectoid zone after case carburizing existed previous to the ingot, *i.e.*, it was in the steel-furnace practice.

In this connection, it was found that the results to be obtained in carburizing and hardening varied with different heats of steel as made. This seemed to offer a means of checking and eliminating this class of steel as a steel of carburizing quality, as it only became necessary to carburize a section of a small test ingot poured from the ladle. This test was finally adopted after careful checking. It was found that if this small test ingot, poured from the middle of the heat, was unsatisfactory, apparently the whole heat was unsatisfactory.

On a more extended checking of many samples from different heats, of both electric and basic open-hearth steel, it was found that the condition which caused the instability of the pearlite in the hypereutectoid zone exists not only in different heats but in different parts of the same heat; although if indications of very abnormal steel are present in part of a heat it appears likely that most of the heat is affected.

Steel that shows indication of breaking down of the pearlite in the hypereutectoid zone after carburizing will harden successfully if this condition is not too far advanced, but the results obtained will not be as good so those shown by a really good steel. Abnormal steel will not respond so well to the quenching and it is difficult, if not impossible, to develop in hardening a satisfactory case. It is also true that the case obtained with abnormal steel will be of less depth than with normal steel, and will be more variable in character; see Fig. 20–23. In fact, most of the variation in carburizing results obtained when work is packed in a bone-base compound, in the same carburizing pot, can be ascribed to variation in the quality of the steel. This is an important fact and has been most noticeably true in the past few years.

When determining microscopically whether a certain steel is normal or abnormal, it should be noted that the hypereutectoid zone is necessary to develop the breaking down of the pearlite; and while the gradation zone of the abnormal steel can easily be distinguished from the gradation zone

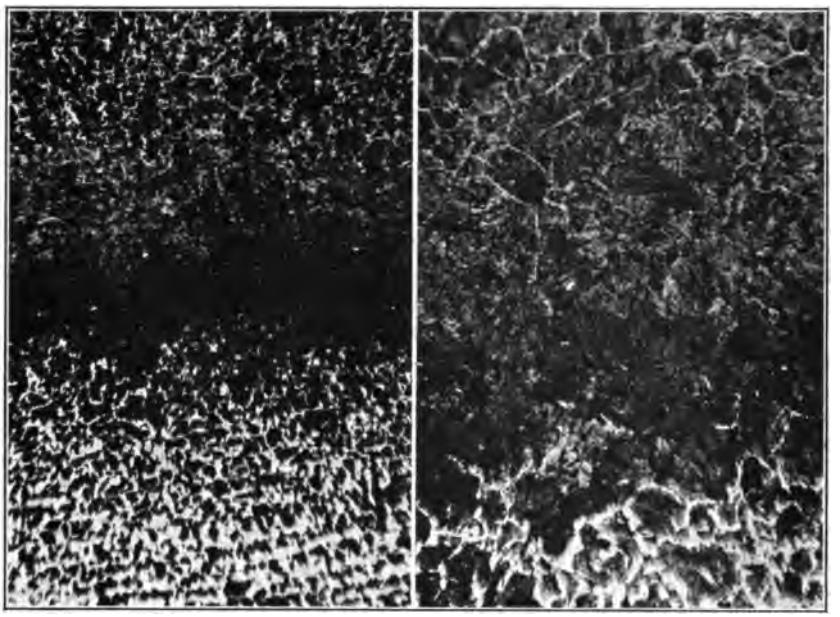


FIG. 20.—ABNORMAL STEEL. × 50. FIG. 21.—NORMAL STEEL. ×50.

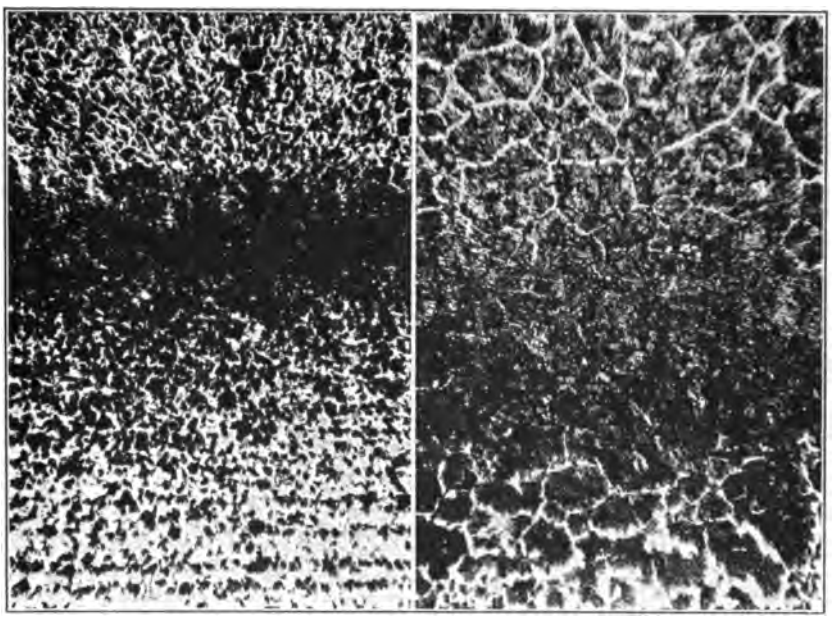


FIG. 22.—ABNORMAL STEEL. × 50. FIG. 23.—NORMAL STEEL. × 50.

SHOWING VARIATION IN CASE DEPTH AND QUALITY OF NORMAL AND ABNORMAL STEEL PACKED TOGETHER IN SAME CARBURIZING POT.

of normal steel after carburizing, the eutectoid zone shows little difference, the pearlite in the abnormal steel apparently having a slight tendency to become coarsely lamellar. The presence of cementite, however, apparently facilitates the breaking down of the pearlite and hence the higher the carbon concentration (the greater the amount of excess cementite), the more complete will be the breaking down of the pearlite. Therefore, carburizing compounds that produce a very high-carbon case will indicate more clearly whether the steel is normal or abnormal.

In checking the carbon content and the gradation of the carbon from the surface to the core, special test rings are made, as shown in Fig. 24.

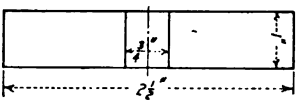


FIG. 24.

Cuts are carefully taken from the surface in steps of 0.005 in. (0.127 mm.) each. The sides are first cut away to a depth of 0.125 in. (3.175 mm.) to prevent the carburized faces from affecting the check. The turnings from each 0.005 in. layer are separately analyzed for carbon content by the combustion method. Checking by this method shows the carbon content of the hypereutectoid zone of the abnormal steel to be the same as, or if anything greater than, that of the corresponding zone of normal steel. Repeated analyses could determine no marked difference in the manganese, sulfur, or phosphorus content of the normal and abnormal steel.

In order to determine the fundamental cause of the condition that affected the carburizing results, many experiments were made. The fact that, in an otherwise normal steel, a ghost line through the case after carburizing would cause the pearlite to break down, with a very abnormal structure at this point, would indicate that the segregation of sonims in the ghost lines was a contributing cause. Figs. 25 to 28, show the effect of a ghost line on the case, and the same section etched in hot sodium-picrate solution.

A basic open-hearth steel that contained a considerable number of heavy ghost lines was at hand; this steel offered positive evidence that a ghost line through the case would cause the pearlite to become very unstable and break down entirely in the hypereutectoid zone. This condition was checked many times, the hypereutectoid zone at all places being normal except at those spots where the ghost line persisted. As this was well established, it was necessary to determine what condition peculiar to the ghost-line formation was interfering with the formation of normal pearlite.

In order to determine the effect of non-metallic inclusions, the following test was made: Several holes $\frac{1}{32}$ in. (0.79 mm.) in diameter were drilled in a section of electric-furnace steel from a bar previously checked and found to be normal. The section was 3 in. in diameter by $2\frac{1}{2}$ in. in length and was taken from a hot-rolled bar. These drilled holes were

FIG. 25.—GHOST LINE THROUGH HYPEREUTECTOID ZONE; NOTE COMPLETE PEARLITE DIVORCE. × 200.

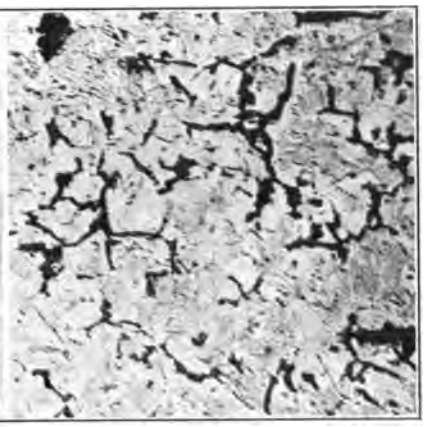


FIG. 26.—SAME AS FIG. 25, USING SODIUM PICRATE ETCH. × 200.

FIG. 27.—GHOST LINE THROUGH HYPEREUTECTOID ZONE. × 100.

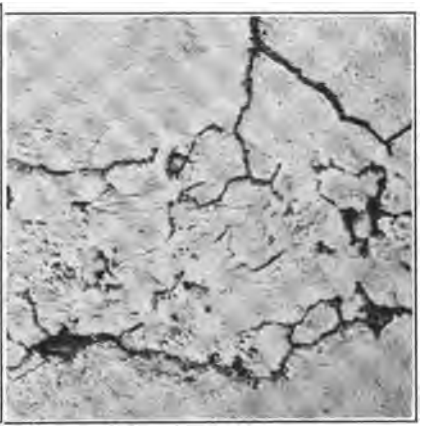


FIG. 28.—SAME AS FIG. 27, USING SODIUM-PICRATE ETCH. × 100.

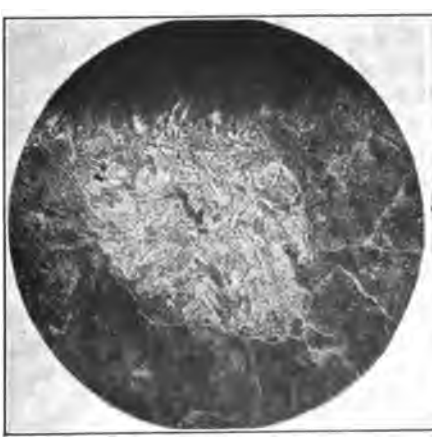


FIG. 29.—MANGANESE-SULFIDE INCLUSION IN HYPEREUTECTOID ZONE. × 100.

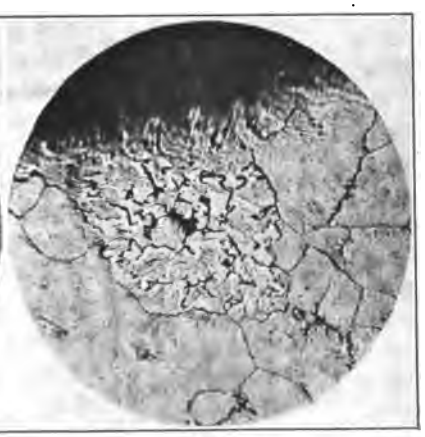


FIG. 30.—SAME AS FIG. 29, USING SODIUM-PICRATE ETCH.

filled with pulverized iron oxide, iron sulfide, and manganese sulfide, and the holes closed by riveting. The piece was forged down to about 5/8 in.

FIG. 31.—OXIDE (MILL SCALE) INCLUSION THROUGH HYPEREUTECTOID ZONE. × 50.

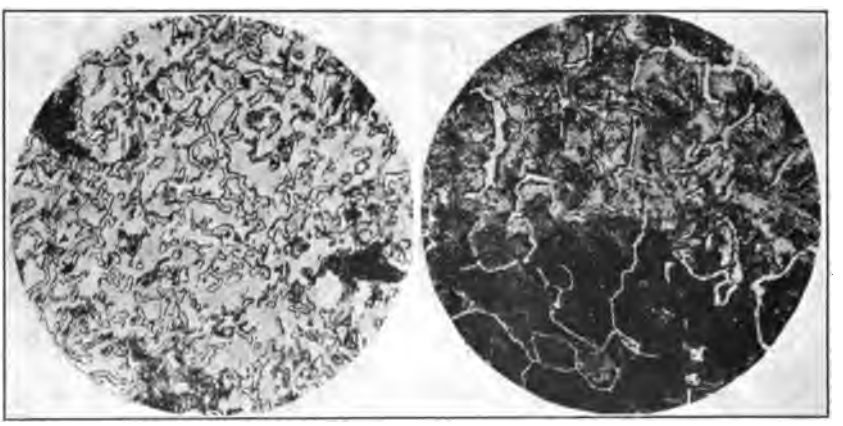


FIG. 32.—HYPEREUTECTOID ZONE OF ELECTRIC STEEL BLOWN WITH OXYGEN; NOTE COMPLETENESS OF PEARLITE DIVORCE. × 200.

FIG. 33.—SECTION OF WELD, HYPEREUTECTOID ZONE; ABNORMAL AND NORMAL STRUCTURE. × 200.

diameter and then reheated to 2200°–2300° F. to fuse the oxide and sulfide, after which it was turned to ½ in. diameter and carburized for 24 hr. at

1700° F. The carburized rod was cut into sections and examined. The results are shown in Figs. 29, 30, and 31. These results indicate simply that impurities dissolved in the steel tend to cause the disintegration of

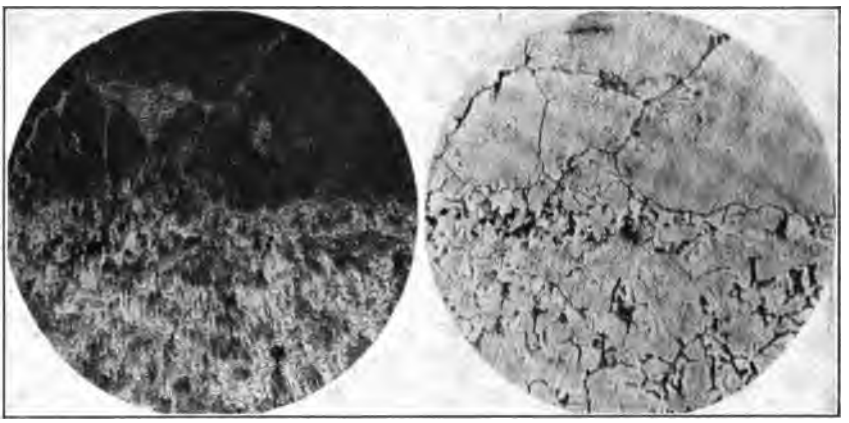


FIG. 34.—HYPEREUTECTOID ZONE (TOP NORMAL, BOTTOM ABNORMAL) STRUCTURE FORGED TOGETHER BEFORE CARBURIZING. × 200.

FIG. 35.—SAME AS FIG. 34, USING SODIUM-PICRATE ETCH.

the pearlite. In the case of iron oxide, the carburization is almost entirely prevented, as could be expected.

As a further check, oxygen was blown on to molten electric-furnace

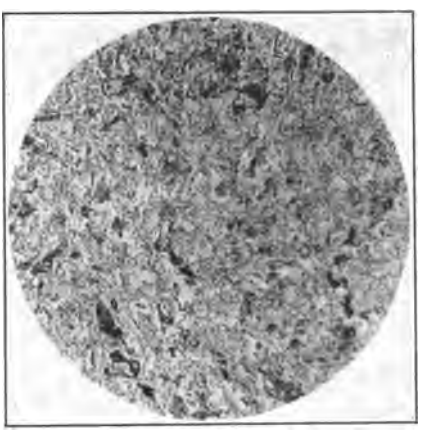


FIG. 36.—SECTION OF NORMAL STEEL SUBJECTED TO OXIDIZING FURNACE GASES AT 2300° F.; HYPEREUTECTOID ZONE AFTER CARBURIZING.

steel in a small ladle, by introducing a stream of oxygen from a commercial oxygen tank. Samples were machined, carburized, and the resultant case examined. The result, Fig. 32, shows the pearlite of the hypereutec-

toid zone to be almost completely broken down and the cementite entirely in the massive state. The steel, after being blown with oxygen while molten, proved to be absolutely worthless as far as case carburizing and hardening are concerned.

Small pieces of normal electric-furnace steel welded together by melting low-carbon welding rod around them, in the oxygen-acetylene flame, were carburized and examined. As shown, Fig. 33, the melted welding rod, which was subjected to a severe oxidizing action by melting, proved to be very abnormal whereas the electric-furnace steel proved to be perfectly satisfactory.

By taking a small sample of electric-furnace steel just after melting down, before any refining has taken place, and forging a piece of cold normal steel into it, when it had reached a temperature of 1800°–2000° F., it was possible to check the result of carburizing intimately connected pieces of unfinished and finished steel and compare the results. The

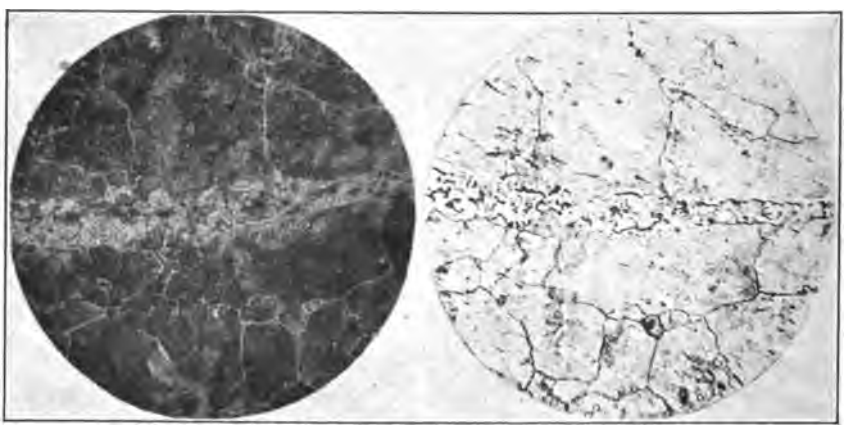


FIG. 37.—SURFACE CRACK THROUGH HYPEREUTECTOID ZONE. × 100.

FIG. 38.—SAME AS FIG. 37, USING SODIUM-PICRATE ETCH. × 100.

unfinished steel in this case was considerably lower in carbon and manganese than the finished steel. The results, Figs. 34 and 35, show how distinctly different are the hypereutectoid zones of the two steels.

It was also determined that a steel that would give a normal case after carburizing could be converted to an abnormal steel merely by heating to 2300° F. or over for from 1 to 2 hr. in an oxidizing atmosphere. This result, it is supposed, is due to burning and penetration of the oxygen into the steel. Figs. 36, 37, and 38 show the effect of scale rolled into a surface during hot working, on the structure of a normal steel.

It was also found that, in general, the steel produced in the 6-ton Heroult electric furnaces at the Timken plant, melting down cold scrap, reacted as abnormal steel until the ferrosilicon had been added, although

some heats were much more abnormal than others. As the heat progressed, the steel improved as far as the carburizing check was concerned, finally becoming normal after adding the deoxidizer. Some heats were

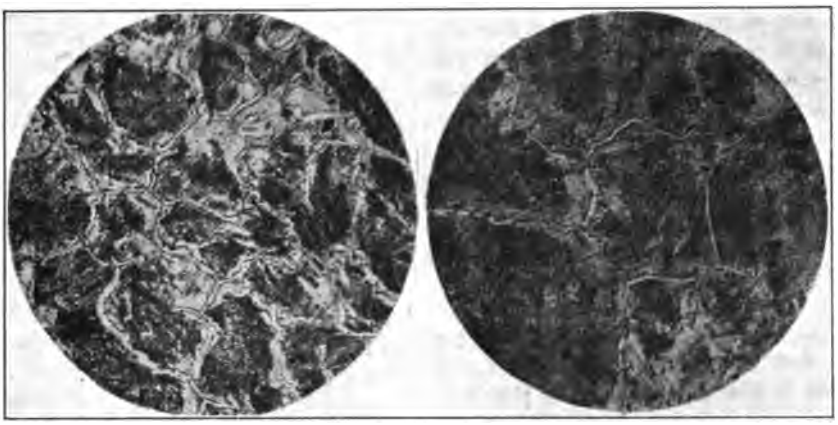


FIG. 39.—HYPEREUTECTOID ZONE, FORGED ELECTRIC-STEEL INGOT POURED IMMEDIATELY AFTER MELTING DOWN OF CHARGE. × 100.

FIG. 40.—SECOND STAGE OF SAME HEAT AS SPECIMEN SHOWN IN FIG. 39, FIRST ADDITIONS MADE AND SECOND SLAG SHAPING UP. STILL SHOWS PEARLITE DIVORCE. × 100.

found, however, that reacted normally just after melting down; see Figs. 39 to 42.

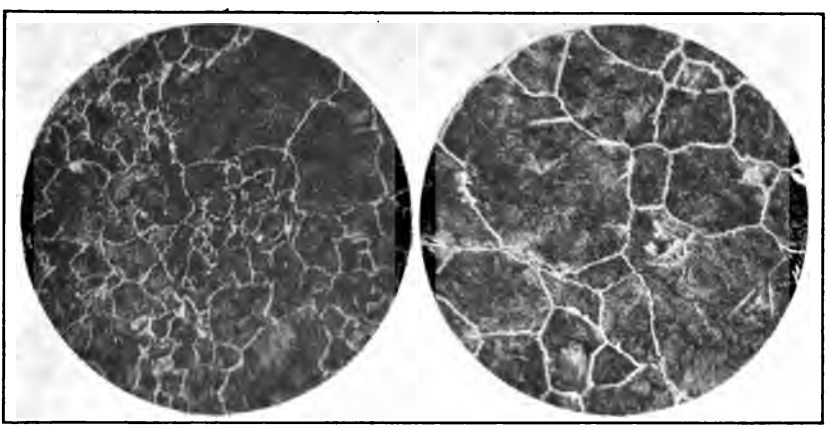


FIG. 41.—THIRD STAGE OF SAME HEAT AS SPECIMEN SHOWN IN FIG. 39; FERRO-SILICON ADDED; NEARLY NORMAL. × 100.

FIG. 42.—FINISHED HEAT, NORMAL STEEL. × 100.

In order to check the results obtained by the writers, samples of steel with a statement of conditions under which they were obtained were

submitted to Sauveur and Boylston for independent criticism. After investigating, they reported in effect that the evidence submitted indicated that the carburizing results were influenced by the condition of the steel as made and offered to submit for check, samples of steel used by Mr. Boylston[1] in connection with his work on the value of different deoxidizers. This was done, and it was found that the samples from the ingots deoxidized with ferromanganese, ferrosilicon, and ferrocarbotitanium gave a normal hypereutectoid zone after carburizing, while the samples from ingots deoxidized with carbon-free ferrotitanium and aluminum gave an abnormal hypereutectoid zone, indicating a different condition of the steel. Figs. 43 and 44 show an abnormal and a normal case with different deoxidizers. All samples on this test were packed in the same carburizing pot.

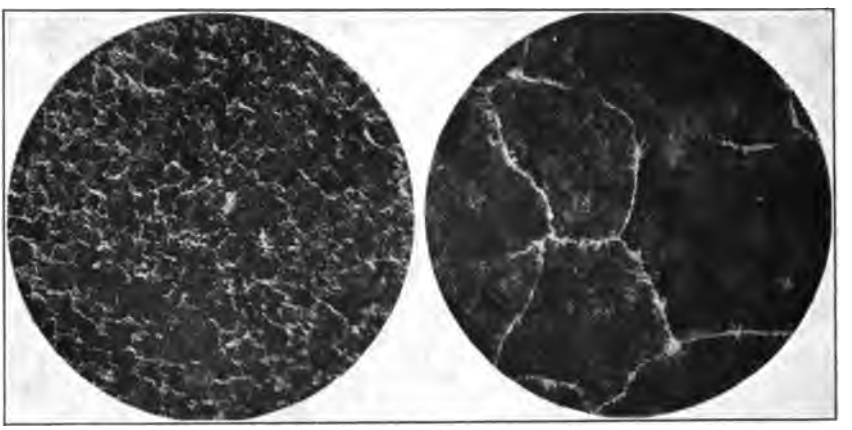


FIG. 43.—BOYLSTON TEST PIECE, HYPEREUTECTOID ZONE; SPECIMEN FROM INGOT DEOXIDIZED WITH ALUMINUM. × 200.

FIG. 44.—BOYLSTON TEST PIECE. HYPEREUTECTOID ZONE; SPECIMEN FROM INGOT DEOXIDIZED WITH FERROMANGANESE. × 200.

Etching, by cupric reagents, of the free ferrite formed by the breaking down of the hypereutectoid zone of abnormal steel showed no indications of phosphorus concentration. It is believed by the writers that the carburizing (24 hr. at 925° C.) is sufficient to permit of the phospho us diffusion, as all efforts to obtain evidence of segregated phosphorus after carburizing have failed, although the ghost lines still persist.

Figs. 45 and 46 show a manganese-sulfide inclusion in the hypereutectoid zone after carburizing, with no evidence of change in the normal lamellar pearlite. The fact that manganese sulfide introduced into normal steel (Fig. 29) caused the breaking down of the pearlite after carburization in the portion of the metal surrounding the inclusion is not

[1] Iron and Steel Inst. *Carnegie Schol. Mem.* (1916) **7, 102.**

a necessary contradiction of the result indicated by Fig. 45, for in introducing the sulfide into the steel, considerable air (oxygen) was introduced at the same time.

The effect of slag and silicates on the carburizing results has not been fully investigated, it being evident that these sonims could not be a principal cause. It was determined that, in a 75-ton, basic, open-hearth heat, blooms from all sections of the heat were abnormal, indicating that the cause of the abnormal steel was present in all parts of the heat, a condition not likely to be true if slag or silicates were a principal cause.

The investigations by Stead,[2] Whiteley[3] and McCance[4] have indicated that dissolved oxide is one of the most probable causes of ghost lines. LeChatelier and Bogitch[5] have apparently proved that this is the case,

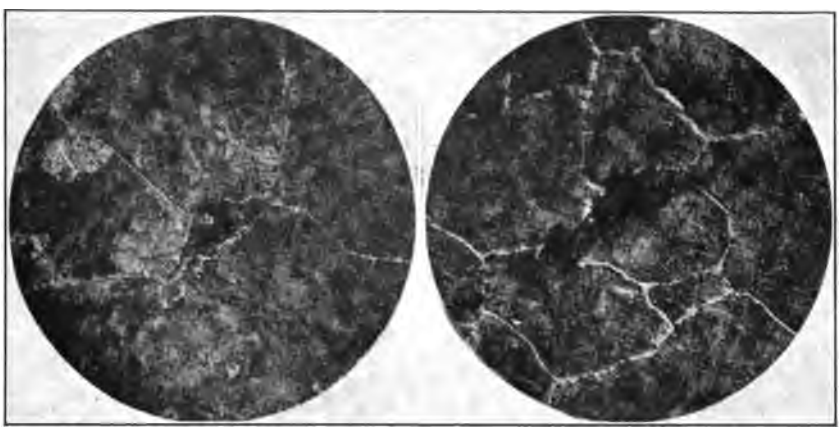


FIG. 45.—MANGANESE-SULFIDE INCLUSION IN HYPEREUTECTOID ZONE OF NORMAL STEEL. × 200.

FIG. 46.—MANGANESE-SULFIDE INCLUSION IN HYPEREUTECTOID ZONE OF NORMAL STEEL. × 200.

which results are checked by the evidence obtained by the writers that ghost lines are the effect of the same cause as abnormal steel, namely dissolved oxides.

This is more or less substantiated by the facts that unfinished steel is, as a rule, abnormal and that the addition of the deoxidizer (manganese, silicon, etc.) is necessary to produce normal low-carbon steel. Why dissolved iron oxide should cause the divorce of the pearlite of the hypereutectoid zone is a subject for independent investigation; the most appealing explanation is that the solubility of the cementite in gamma iron is decreased by the presence of the dissolved oxide and hence it is more

[2] *Jnl.* Iron and Steel Inst. (No. I, 1918) and (No. I, 1920).
[3] *Jnl.* Iron and Steel Inst. (No. I and II, 1920).
[4] *Jnl.* West of Scotland Iron and Steel Inst.
[5] *Rev. de Mét. Mem.* (1919) **16.**

easily precipitated to the crystal boundaries on cooling through the critical range. The extent to which the cementite would be rejected to the crystal boundaries would depend on the amount of the oxides in solution as well as on the amount of the cementite and the speed of cooling.

It has usually been assumed, and investigations made by Howe and Levy[6] would indicate, that slow cooling through the critical range was the primary cause of the pearlite divorce. They also point out that with a maximum temperature of 900° C. the pearlite formed on slow cooling is more stable and much coarser than when the initial temperature is 800° C. This, as regards stability of the pearlite at the different initial temperatures, is checked by the investigations of Honda and Saitô,[7] who show that at 900° C. the pearlite formed on slow cooling is lamellar in structure. This cannot be universally true, for the writers have examined hundreds of specimens of steel corresponding in carbon content to the 1.20-per cent. carbon steel of Honda and Saitô in which the pearlite had divorced completely to form massive cementite and free ferrite, after cooling slowly from 925° C. The results obtained by Honda and Saitô and by Howe and Levy coincide exactly with results obtained by us with what we have termed normal steel and it is our opinion that the investigations referred to have been made on steels of this quality.

Brearly[8] illustrates a condition identical with that met with in abnormal steels and ascribes the cause of the formation of massive cementite to low manganese content. Just how manganese is the cause of this condition is not explained but it is the writers' belief that the connection between the low manganese content and the divorcing of the pearlite of the hypereutectoid zone after carburizing is indirect, it being generally true that one result of a poorly deoxidized heat is loss of manganese content. It has been our experience that manganese content is an indication of the character of the steel, and that steel in which the manganese content is close to the minimum chemical specification is not so well made as steel in which the manganese content approaches the maximum specification for the element. This is true because manganese is added (as ferromanganese) to produce a predetermined percentage of that element in the finished heat, and when the finished content is less than that aimed at, it is assumed that the loss is due to the presence of oxides in the bath. It is possible that the loss in manganese may be compensated for by more complete deoxidation of the steel and hence the resulting steel might be of excellent quality. Unless otherwise noted, all steel carburized in connection with this investigation contained manganese of from 0.35 to 0.65 per cent.

[6] *Jnl.* Iron and Steel Inst. (No. II, 1916).
[7] *Jnl.* Iron and Steel Inst. (No. II, 1920).
[8] "Case Hardening of Steel," 60.

From the foregoing, it would seem that the extent to which deoxidation takes place in finishing steel in the melting furnace has an important bearing on results obtained after case carburizing and hardening; and, conversely, the results obtained in case carburizing constitute a check on the extent of deoxidation of the low-carbon steel used for carburizing purposes.

If it be true that a poorly deoxidized heat of low-carbon steel will, when carburized, produce a case in which the pearlite of the hypereutectoid zone is more or less unstable, depending on the amount of oxides included or in solution, we have a method of inspection of this class of steel that will indicate under what conditions the steel was made.

While the writers have successfully adopted this method of checking steel for case carburizing, it has often been difficult to decide at just what indication of the divorcing of the pearlite to draw the line. There is not the slightest doubt that the structure of the case shown in Fig. 4 will not form normal martensite under the most favorable hardening conditions, but there is an intermediate stage between this and normal steel that will form martensite under proper hardening conditions but is more likely to develop soft troostitic areas than normal steel. As the presence of dissolved oxide apparently renders the pearlite of the hypereutectoid zone after carburizing unstable, with consequent formation of a very unstable martensite in hardening, it would seem reasonable that the presence of excess dissolved oxides would have the same effect on high-carbon tool steel, making such a steel difficult to harden without soft areas. This condition would explain the often mysterious failures of some tool steels to harden properly and indicates the necessity of insuring, in the production of high-grade tool steel, that the greatest care be taken in the melting practice, a fact generally well known. Those processes using first-quality scrap for the furnace charge and melting in a non-oxidizing atmosphere should give a superior tool steel. Whether the beneficial effect of an alloy on the case-carburizing results is caused by the greater care generally taken in the production of alloy steel or by the deoxidizing qualities of the added element itself, or both, is not known.

In order to check our method of inspection, samples from four heats of low-carbon basic open-hearth steel from one of the mills supplying us with open-hearth steel were submitted for check, of which three were accepted and one rejected. It developed that the three accepted had been carefully made under the personal supervision of the open-hearth superintendent, whereas the rejected heat had been deliberately picked out as poorly made. The success of this check resulted in obtaining the coöperation of the open-hearth operating department and an improvement in the quality of the steel made for carburizing purposes.

On checking steel for case carburizing from another mill, it was admitted by the producer that the steel rejected was not originally intended

for our use, but being within our chemical specification it had been diverted to our order. It was of "merchant bar" grade and showed up unusually poor when checked. It is not difficult to realize that the carburizing check is probably the only one that would have caused its rejection.

In conclusion the writers desire to express their appreciation for the assistance and encouragement extended them by M. T. Lothrop, works manager of The Timken Roller Bearing Co., whose interest and direction have been of the greatest value.

DISCUSSION

H. J. FRENCH* and L. JORDAN,* Washington, D. C. (written discussion).—The data and explanations given are of considerable interest and importance. The authors have shown a number of differences in behavior in heat treatment between certain heats of electric-furnace and open-hearth steels of similar compositions as ordinarily determined, and have also traced the sources of such differences to melting and refining practices. They have not, however, so clearly shown that oxygen is the controlling factor in producing the observed effects and it is to be regretted that no values are given for the oxygen content of steels designated as normal and abnormal.

In view of this fact, any examples of differences observed in the heat treatment of electric-furnace and open-hearth steels carrying equal proportions of those elements usually specified, notably carbon, manganese, phosphorus, sulfur and silicon, but showing variations in the proportions of gases present, should be of particular interest. The case to be cited is that of silico-manganese spring steels in which some of the observed differences in structure are similar to those shown by the authors.

Based on observations made in the heat treatment of hundreds of tons of this type of material the following fact was stated at the Philadelphia meeting of the American Society for Steel Treating, September, 1920. When silico-manganese steel made in the open hearth has the same proportions of carbon, manganese, phosphorus, sulfur, and silicon as an electric-furnace product and both alloys are hardened in the same manner, they regularly require different tempering temperatures to produce the same Brinell hardness.

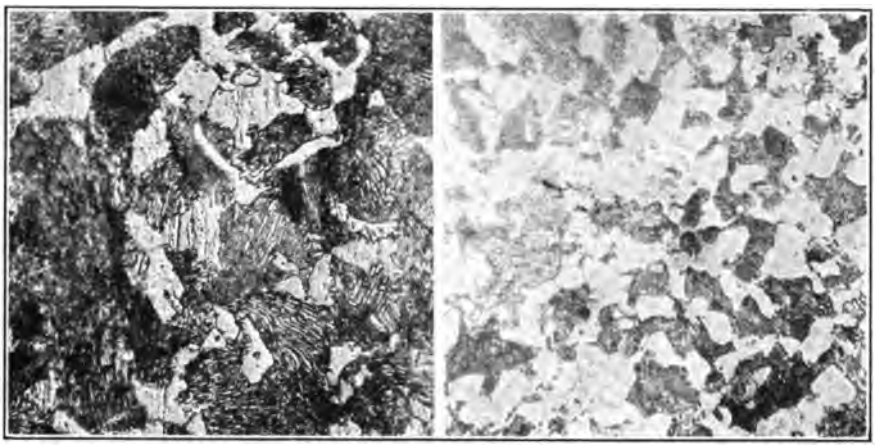
Samples of typical electric-furnace and open-hearth heats of such spring steels were obtained and subjected to various heat treatments. The compositions and tensile-test results are given in Tables 1 and 2, while typical microstructures are shown in Figs. 47, 48, and 49.

It will be noticed that the difference in structure between rolled electric-furnace and open-hearth silico-manganese steels (Figs. 47 *a* and *b*)

* Physicists, Bureau of Standards.

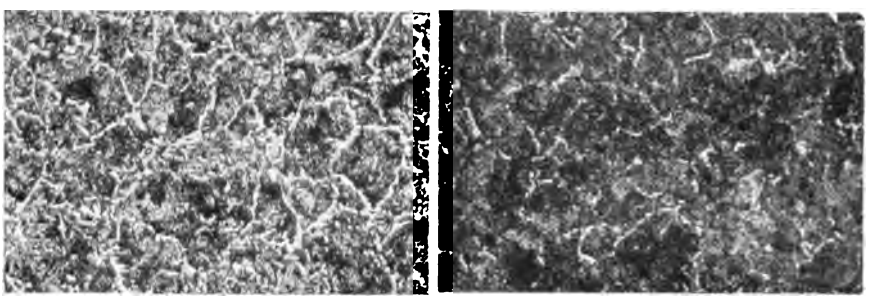
are much like those observed in the hypereutectoid zone of carburized normal (electric-furnace) and abnormal (open-hearth) steels shown in Figs. 1 and 2.

The greater continuity of the excess ferrite of the normal carbon (electric-furnace) steel when compared with the abnormal (open-hearth)



a *b*

FIG. 47.—ROLLED ELECTRIC-FURNACE AND OPEN-HEARTH SILICO-MANGANESE STEEL. *a* ELECTRIC STEEL. *b* OPEN-HEARTH STEEL. × 500. ETCHED WITH 2 PER CENT. NITRIC ACID IN ALCOHOL.



a *b*

FIG. 48.—NORMALIZED ELECTRIC-FURNACE AND OPEN-HEARTH SILICO-MANGANESE STEELS. *a* ELECTRIC STEEL; *b* OPEN-HEARTH STEEL. 1800° F., OIL; 1650° F. AIR. × 100. ETCHED WITH 2 PER CENT. NITRIC ACID IN ALCOHOL.

heats, as shown in Figs. 6 and 7, is similarly shown for the normalized spring steels first quenched from a high temperature, in Figs. 48 *a* and *b*.

Differences in structure persist in these alloy steels when they are quenched and tempered in the ordinary manner and also when subjected to special heat-treatments, as shown in Fig. 49. In each case the electric-furnace and open-hearth heats were treated simultaneously and in the

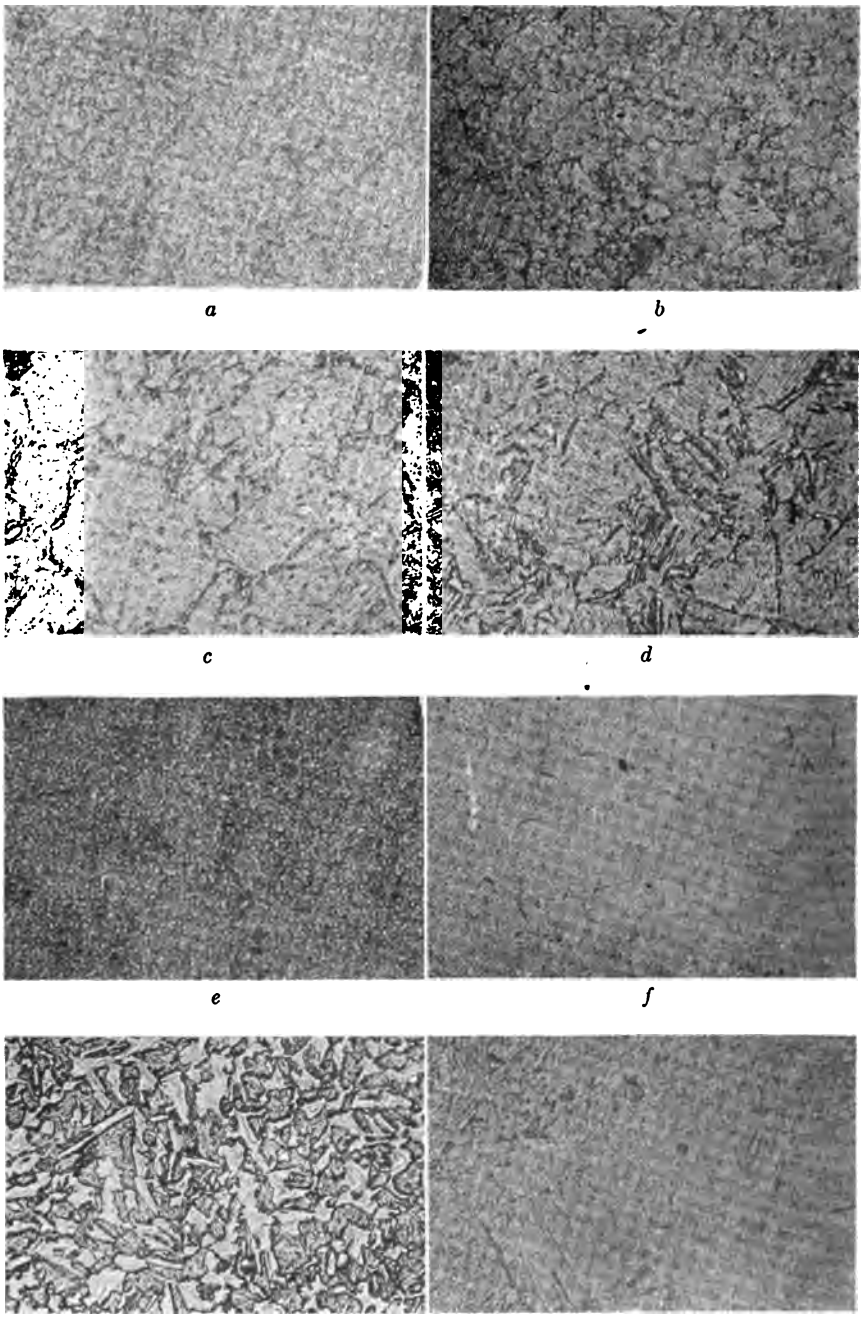


FIG. 49.—QUENCHED AND TEMPERED ELECTRIC-FURNACE AND OPEN-HEARTH SILICO-MANGANESE STEELS. *a* ELECTRIC STEEL. × 100. *b* OPEN-HEARTH STEEL. × 100. *c* ELECTRIC STEEL. × 500. *d* OPEN-HEARTH STEEL. × 500. 1650° F., OIL; 650° F., AIR. *e* ELECTRIC STEEL. × 100. *f* OPEN-HEARTH STEEL. × 100. *g* ELECTRIC STEEL. × 500. *h* OPEN-HEARTH STEEL. × 500. 1800° F., OIL; 1650° F., OIL; 650° F., AIR. ETCHED WITH 2 PER CENT. NITRIC ACID IN ALCOHOL.

same manner. Photomicrographs *a* and *b* show the more regular and complete ferrite envelopes existing in the electric-furnace product for steels quenched from 1650° F. and tempered at 650° F. When these alloys were first subjected to a normalizing quench and then treated as above, the structures shown in *g* and *h* were obtained.

It is evident from these photomicrographs that the structures obtained in the heat treatment of the electric-furnace spring steel are different from those obtained after application of the same treatments to the open-hearth steel and that in a number of instances these differences are quite similar to those observed by the authors in low-carbon steels.

The proportions of carbon, manganese, phosphorus, sulfur, and silicon present in both types of spring steel are practically identical and but one appreciable difference in composition is revealed in results of analysis for oxygen and nitrogen[9] (Table 1). The nitrogen contained in the

TABLE 1.—*Composition of Steels as Received*

Steel	Process	Composition, Per Cent.							Sample No.
		C	Mn	P	S	Si	N_2	O_2	
A	Electric.....	0.53	0.77	0.022	0.014	2.09			A26
							0.0046		A16
							0.0045	0.023	A 2
B	Open-hearth....	0.54	0.77	0.017	0.022	2.03			B29
							0.0020	0.028	B32
							0.0028	0.028	B 1

electric-furnace steel is approximately twice that in the open-hearth. No difference in oxygen content is observed.

In view of the importance attached to oxygen content by the authors

[9] The values given for the oxygen content of these steels were obtained by the Ledebur method following the procedure described by Cain and Pettijohn in Bureau of Standards *Tech. Paper* 118. It is generally recognized that this method does not determine all the oxygen in all the forms in which it is possibly present in a steel; values for oxygen are particularly liable to be low in the case of steels containing more than small amounts of carbon. Comparative results of significance are obtained, however, by the application of this method to steels of similar composition.

The nitrogen was determined by a modified Allen method, practically as described by Tschischewski: *Jnl.* Iron and Steel Inst. (1915) **92**, 47–90. This method determines only the combined nitrogen (sometimes designated as "nitride" nitrogen) present in the steel.

Hydrogen, carbon dioxide, and carbon monoxide were determined in the spring steels as rolled. No marked differences were found between the electric-furnace and open-hearth steels in the amounts of these gases. Analyses for these gases were made by a vacuum-fusion method developed at the Bureau of Standards.

and the difference in nitrogen content found in the original silico-manganese steels, both oxygen and nitrogen were determined on samples heat-treated in different ways; the results are summarized in Table 2.

The treatments to which the alloys were subjected may be divided into two classes. The first, in which a normalizing or hardening tempera-

TABLE 2.—*Proportions of Oxygen, Nitrogen, and Tensile Properties of Electric-furnace and Open-hearth Silico-manganese Steels under Various Heat Treatments*

Condition or Heat Treatment	Heat and Sample No.	Tensile Strength, Lb. per Sq. In.	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.	Gas Content,[a] Per Cent.		Remarks
					O_2	N_2	
As rolled, open-hearth...	B 1	129,800	20.0	43.8	0.028	0.0028	Average N_2, 0.0024 per cent.
As rolled, open-hearth...	B32				0.028	0.0020	
As rolled, electric.....	A 2	126,300	19.0	40.0	0.023	0.0045	Average N_2, 0.0046 per cent.
As rolled, electric.....	A16					0.0046	
	Open-hearth, Regular Treatment A						
1650° F. oil; 900° F.....	B 2	190,200	10.0	36.1	0.024	0.0031	
	B 5	196,000	12.0	34.3			
	Open-hearth, Special Treatment A						
1800° F. oil; 1650° F. oil; then 900° F.....	B19	204,500	10.0	24.8	0.026	0.0030	
	Electric Steel, Regular Treatment A						
1650° F. oil; 900° F.....	A 5	201,600	9.5	26.1	0.025	0.0063	
	Electric Steel, Special Treatment A						
1800° F. oil; 1650° F. oil; then 900° F.....	A31	200,000	9.0	28.8	0.030	0.0102	
	Open-hearth, Regular Treatment B						
1650° F. oil; 650° F.....	B 4	327,000	4.0	14.2			
	Open-hearth, Special Treatment B						
1800° F. oil; 1650° F. oil; then 650° F.....	B15	320,000	4.0	13.6			
	Electric Steel, Regular Treatment B						
1650° F. oil; 650° F.....	A 4	260,000	1.0	2.8	0.029	0.0066	Average N_2 in electric steel, regular treatments, 0.0064 per cent.
	Electric Steel, Special Treatment B						
1800° F oil; 1650° F. oil; then one 650° F.....	A14	313,000	2.5	8.8			
	Electric Steel, Special Treatment C						
1800° F. oil; then 1650° F. air.						0.0092	Average N_2 in electric steel, special treatments, 0.0097 per cent

[a] All values reported are averages of at least duplicate determinations.

ture of 1650° F. was used, may be referred to as a "regular treatment;" the second, in which a preliminary heating to 1800° F. (designed to break up refractory structures) was used, may be classed as a "special treatment." This was in all cases followed by a regular treatment.

Throughout the whole series of determinations no appreciable differences in oxygen content are evident either between various treatments or between the two types of steel.

The nitrogen content of the untreated open-hearth steel remains practically constant at 0.0028 per cent. and is independent of the different heat treatments applied; that of the untreated electric-furnace steel, which was approximately twice that of the untreated open-hearth (0.0046 per cent.), increases to 0.0064 per cent. when the regular heat treatment is applied and this value is again raised to 0.0097 per cent. when the steel is subjected to the special treatment. This latter value is about the same, whether the treatment subsequent to the preliminary high-temperature quench is hardening and tempering or normalizing.

Probably these differences indicate a change in the condition of a portion of the nitrogen as it is difficult to believe that the heat treatment, as carried out, could change the total amount of this element in the steel.[10]

No definite statements should be made, without further and more extended investigation, concerning the relation between nitrogen contents and changes in tensile properties in electric-furnace and open-hearth steels resulting from the special normalizing quench. It is to be noted, however, that after special treatments recorded in Table 2 the tensile properties of the open-hearth and electric-furnace steels are in general more uniform than after the more simple regular treatment.

It is appreciated that any statements based on work with silicomanganese steels are not necessarily applicable when considering the low-carbon steels, except in so far as it is justifiable to draw inferences by analogy. The writers' purpose in presenting their results is to show that differences in structure similar to those presented by McQuaid and Ehn are found in other steels without change in the oxygen content. They cannot, however, at the present time, correlate nitrogen variations with any structural or physical characteristics of the steels tested.

In conclusion, attention is invited to the fact that steels of the same chemical composition, in so far as the elements usually determined are concerned, require variations in heat treatment in order to produce similar physical properties. This applies to comparison between heats made by the same type of process as well as to comparisons between steels produced by different processes.

The results presented by the authors may certainly be considered as further evidence of differences in heat-treatment properties in a particular field, but to demonstrate the relation of the gas content to any such changes is at the present time a difficult matter.

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[10] See footnote 9. The method of analysis used is believed to give only the combined nitrogen.

W. J. PRIESTLEY,* South Charleston, W. Va.—It would be interesting to know some of the other characteristics of that electric steel, also to have more data about the open-hearth steel with which that electric steel was compared.

H. J. FRENCH.—Do you mean the number and distribution of non-metallic materials?

W. J. PRIESTLEY.—Yes; if specimens of that steel are available, it would probably be well to have photomicrographs taken to show the inclusions; also, to have a chemical analysis made.

H. J. FRENCH.—We have the chemical analyses.

W. J. PRIESTLEY.—It would also be well to draw pieces of the same steel at a higher temperature so as to get greater stretch and greater ductility.

H. J. FRENCH.—These steels were examined as received and under various treatments without etching, and there was no evidence, either longitudinally or transversely, of many more sonims in one heat than in the other. The table and the results given do not represent all the tests made. The reason other heats were not included in this discussion was, one of the steels contained about 0.04 per cent. phosphorus, whereas the two for which the results were given contained about 0.02 per cent. Another heat contained approximately twice the amount of sulfur and it was desired to keep out of the results presented any more variations in the chemical compositions than was necessary.

The exact composition of the steels for which results are given is as follows:

	CARBON, PER CENT.	MANGANESE, PER CENT.	PHOSPHORUS, PER CENT.	SULFUR, PER CENT.	SILICON, PER CENT.
Electric Steel	0.53	0.77	0.022	0.014	2.09
Open-hearth Steel	0.54	0.77	0.017	0.022	2.03

In addition to making determinations for oxygen and nitrogen on these heats, hydrogen, carbon dioxide, carbon monoxide and total gas, as obtained by the fusion method developed at the Bureau of Standards, were determined and no marked differences were obtained, with the exception of the nitrogen present in the samples.

M. H. SCHMID,† Canton, Ohio (written discussion).—When the investigations on the effect of quality of steel on case-carburizing results were concluded, and they were preparing their paper, Messrs. McQuaid and Ehn invited the writer to supplement their work by further investigations, with reference to special and alloy steels produced by the United Alloy Steel Corpn. Since that time experiments have been

* Steel Superintendent, U. S. Naval Ordnance Plant.

† Metallurgical Engineer, United Alloy Steel Corpn.

conducted on straight carbon forging steels and commercial alloy steels, comprising nickel, chromium, chrome-vanadium and chrome-molybdenum, high-carbon alloy steels, and chrome-tungsten magnet steels.

It has been shown that dissolved oxides in plain carburizing steel cause a structure in which it is impossible to retain the normal martensite after quenching, and that after carburizing the detection of this condition microscopically is simple; fine lamellar pearlite with crystal boundaries of cementite indicating relative freedom from dissolved oxides, and part broken down massive cementite and free ferrite indicating excessive quantities of dissolved oxides.

Successful applications of this method on high-carbon and alloy steels involve the development of structures that indicate relative amounts of dissolved oxides, and such study and correlation with service tests as will reliably indicate the suitability of such material for the purpose in question. Such tests as have been made on various alloy steels indicate that the evidence obtained will not be so simple in its interpretation as in the case of plain carburizing grades, and in many cases prolonged study and experience will be necessary to determine microscopically whether the percentage of dissolved oxides is sufficient to prevent a satisfactory response to the subsequent thermal manipulations required in the development of ultimate physical properties. However, it is reasonable to assume that modifications and refinements in mechanical details covering various types will result in the attainment of more positive indications and that the human element will therefore be a less important factor.

Tests on special steels from different sources of manufacture and representative of various conditions have been conducted in the laboratories of the United Alloy Steel Corpn. Some of the problems have been studied jointly with McQuaid and Ehn and others independently. The following is a brief resume of the investigations made in this laboratory

Steels of approximately 0.50 and 1.00 per cent. carbon, which did not harden uniformly when water-quenched for small parts made from the first type, and when oil-quenched for springs manufactured from the second, were investigated. Characteristic abnormal structures were developed in the cases where the material would not harden. It was noticeable, however, that such portions of the same heats as processed satisfactorily showed approximately normal structures.

Investigations on nickel steels covered pinions made from a carburizing type containing 0.5 per cent. nickel, in which soft spots developed after water hardening, and automobile drive shafts made from 0.40-per cent. carbon, 3½-per cent. nickel steel, on which in some cases a Brinell hardness of 512 was obtainable after an oil quench, while other shafts from the same furnace charge showed a Brinell hardness as low as 321. Various carburizers and heat treatments were tried on the pinions without

success. In each instance the microscopic examination showed but normal amounts of undissolved oxides, sulfides and silicates, with fairly pronounced banding, but not sufficient to determine the cause of the trouble. After carburizing and slowly cooling, microscopic examinations showed conditions characteristic of abnormal steel. The hypereutectoid zone was non-uniform in grain size, with varying amounts of cementite precipitated to grain boundaries, but in every instance showed a decidedly "spotty" structure with the pearlite broken into massive cementite and free ferrite. The hypereutectoid zone in the carburizing grade used for pinions shows the small grain characteristic of abnormal steel, but as would be expected this condition is less pronounced in the higher carbon shaft.

Four types of spring steel were investigated. These tests were run on eleven heats, on which complete records had been kept and showed physical results ranging from average to excellent, for the purpose of determining to just what extent an interpretation of the microscopic evidence could be correlated with physical properties. A chrome-vanadium steel (carbon 0.45 to 0.55 per cent., manganese 0.70 to 0.90 per cent., chromium 0.80 to 1.10 per cent., vanadium 0.15 per cent.) showing exceptional static and dynamic characteristics had an absolutely normal structure in every respect. The same condition existed for a chrome-carbon heat (carbon 0.85 to 1.00 per cent., chromium 0.25 to 0.40 per cent.).

On one type, a heat that showed extreme irregularity in hardness after quenching, presented positive abnormal structure, although the failure of the heat to harden uniformly can be largely attributed to conditions other than those indicated by the test for dissolved oxides. The structures developed in the other heats could not serve as a guide as to relative physical properties, this being especially true with respect to three chrome-molybdenum heats (carbon 0.45 to 0.55 per cent., chromium 0.80 to 1.10 per cent., molybdenum 0.30 to 0.40 per cent.). This, however, should by no means be considered as a condemnation of the method in question, unless we assume that all troubles with steel quality result from dissolved oxides, which assumption is false.

Magnet steels of the following analyses were investigated: carbon 0.80 to 0.90 per cent., chromium 1.90 to 2.10 per cent., tungsten 0.75 to 0.90 per cent. The regular method of cooling after carburizing did not develop the characteristic structures readily recognized as normal or abnormal steel, and it was only by special retardation in cooling that a structure was brought out that could be interpreted as being at all characteristic of the presence of varying amounts of dissolved oxides. Eighteen heats, on which complete records of magnetic tests had been tabulated, were examined. The best heat could be readily selected from the worst by checking magnetic results, but the differences in structures of those

falling between the two extremes in magnetic values were not pronounced. There was, however, a decided difference in banding between the best and the worst heat.

Progressive steel manufacturers of quality products welcome a method of control that goes beyond that available by the prevailing systems of chemical analysis, physical inspection, microscopic examination, etc., which do not in all cases furnish positive assurance of the suitability of a certain product for the particular purpose for which it is intended. The method outlined by Messrs. McQuaid and Ehn offers opportunities of improvement in the product itself and in the selective application of that product. It offers an opportunity for constructive study and experimentation as to the development of the most efficient methods of deoxidation, also for the selective application of heats to meet specific conditions.

Ten open-hearth heats of chrome-carbon steel for automobile drive shafts were made with varying methods of deoxidation but in every other respect the processes were similar; the final operation was heat treatment to produce a minimum elastic limit value of 120,000 lb. per sq. in. Eighteen pieces from each heat were heat treated to facilitate examination for fiber. Representative tests for physical properties and Brinell values were taken from the finished heat-treated product, approximately 100 tensile-strength and 1000 Brinell tests per heat being made. These results were averaged and studied for uniformity. The heats that showed the closest approximation to normal structure, and indicated the minimum amount of dissolved oxides, also gave the best results in physical properties, although such heats did not necessarily show the greatest freedom from fiber. On this work we considered the test for dissolved oxides of practical advantage in determining the most satisfactory method of deoxidizing.

In the manufacture of special steels, especially the alloy grades, the material is given such care in processing that it is doubtful if this test would locate, except in rare instances, material so high in dissolved oxides as to render it unfit for commercial application. There are times, however, when the requirements are so exacting that a test of this nature might be of practical value as a means of restricting the application of steel in particular cases. Unfortunately the time element entering into the carburizing operation is such that it is impossible to obtain final results between the tapping of the heat and the rolling of the ingots, but the information would be available while the heat is still in billet form and it would be possible to divert it to another finished size where desirable. On the other hand there is a possibility of speeding up the carburizing process, through future development, to permit more prompt submission of final results. This test, however, does furnish a means of submitting to the melter positive proof as to improperly melted heats

without awaiting results on the finished product manufactured from the steel.

A. E. WHITE,* Ann Arbor, Mich. (written discussion).—The paper is unusual in that the evidence is circumstantial, yet convincing; it is to be regretted, though, that the quantities of oxygen in the various sections examined were not determined. Those engaged in case-hardening operations have known for some time that certain lots of case-hardened steel would not give a uniformly hardened surface after a quench and a draw. For this failure the heat treater, the maker of the carburizing compound, the forger, and sometimes the steel maker have been blamed. In view of the conclusions of this paper, the steel maker must now become a permanent addition to this group. Perhaps, manufacturers using steel will realize more fully that the higher prices charged by certain mills is for the purpose of meeting the cost of producing steel of the best quality.

It is regretted that no evidence is submitted to show that the steel subjected to a stream of oxygen was normal preceding this treatment. It is assumed that such was the case and that the conclusions drawn were perfectly justified; yet the strength of this statement would have been much increased had direct evidence been submitted. The paper shows that in the vicinity of sulfides, and suggests that in the vicinity of phosphides and oxides, an abnormal structure results if the steel is case hardened; yet the cause of this abnormal structure is not given. We are at first led to believe that the cause is the non-metallic inclusions; then it is shown that in at least one case a manganese-sulfide inclusion did not produce an abnormal structure. I have seen many cases of abnormal structure adjacent to non-metallic inclusions. Is the cause chargeable to non-metallic inclusions, to oxygen, to some other element or compound to which there has been no reference, or to two or more of the conditions named? Though circumstantial, the evidence is none the less conclusive that badly made steel will not carburize uniformly.

H. J. STAGG and S. C. SPALDING, Syracuse, N. Y. (written discussion). We had an experience with an impure steel a few years ago that may be of interest. The steel apparently was not quite as bad as the authors' steels; we found peculiar or abnormal pearlite but did not find any soft spots after hardening. The steel contained 0.15 per cent. carbon, 0.015 per cent. silicon, 0.72 per cent. manganese, 0.103 per cent. phosphorus, and 0.92 per cent. sulfur.

In carburizing this steel we noticed the numerous ghosts present in the core and a peculiar structure in the pearlite of the case. However, as the hardened pieces were apparently all right and we were primarily

* Professor of Chemical Engineering, University of Michigan.

FIG. 50. × 50.

FIG. 51. × 250.
ETCHING REAGENT, 5 PER CENT. NITRIC ACID IN ALCOHOL.

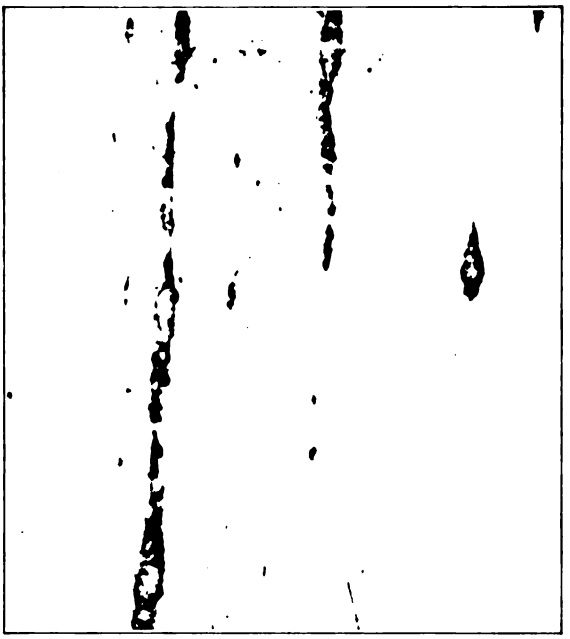

FIG. 52. × 250. UNETCHED.

FIG. 53. × 50.
ETCHING REAGENT, 5 PER CENT. NITRIC ACID IN ALCOHOL.

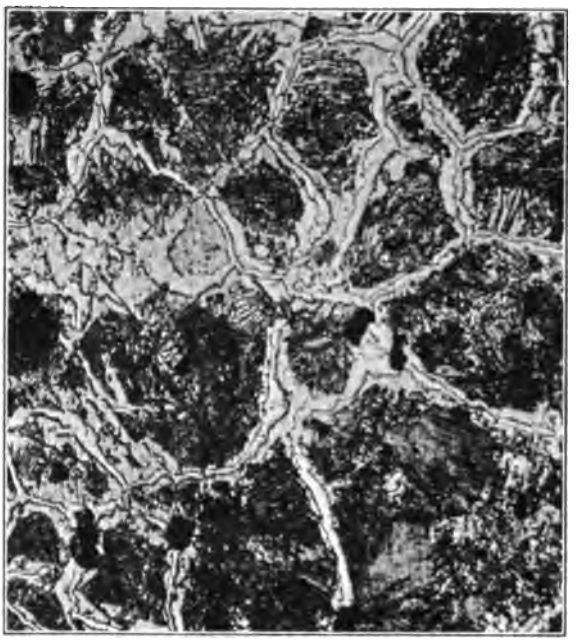

FIG. 54. × 250.

FIG. 55. × 500.
ETCHING REAGENT, 5 PER CENT. NITRIC ACID IN ALCOHOL.

FIG. 56. × 500.

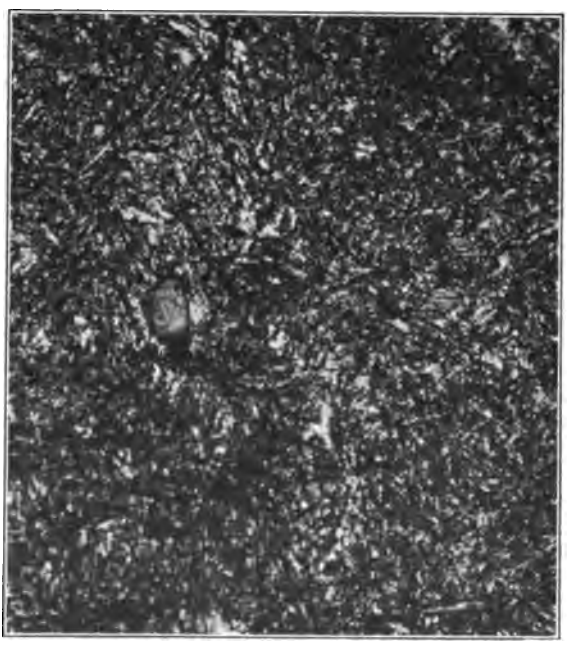

FIG. 57. × 500.
ETCHING REAGENT, 5 PER CENT. NITRIC ACID IN ALCOHOL.

interested in another phase of the carburizing phenomena at that time we did not investigate it any further.

Fig. 50, at 50 diameters, shows the typical ghosts existing in the core. Fig. 51, at 250 diameters, and Fig. 52 unetched, show the wide band of Fig. 50 in a little more detail. Fig. 53, at 50 diameters, shows this band as it goes through the case. The white spot near the outside, followed by a normal eutectoid zone, is not so deep as where the ghost is not present.

Fig. 54, at 250 diameters, taken at the outer edge of the piece in the banded zone, shows the peculiar structure of the pearlite at this point. Fig. 55, at 500 diameters, shows the pearlite as it occurs in the white area of Fig. 53. The cementite in this area appears to occur entirely as boundaries of ferrite grains instead of partly at the boundaries and partly within the grains, as in lamellar pearlite. In some of the grains (see Fig. 54) the normal lamellar pearlite occurs in the center, but at the edges the cementite has apparently left, leaving a border of ferrite. The photomicrograph shows grains in all stages of dissociation of the lamellar pearlite. Fig. 56, at 500 diameters, shows the structure at what was the white spot of Fig. 53 after hardening by a single quench in water from 1500° F. The peculiar pearlite of Figs. 53, 54, and 55, apparently, is transformed into normal martensite by this treatment. Fig. 57, at 500 diameters, shows the structure in a normal portion adjacent to the spot in Fig. 56; the martensites of Figs. 56 and 57 are quite similar.

The specimen on which this work was done was carburized for 20 hr. at 1600° F. and cooled in the pot. A cylinder ¾ in. in diameter and 2 in. long was quenched from 1500° in water and not a single soft spot could be found at any point on its surface.

We have carburized specimens of this steel for time intervals of 5 to 55 hr. at both 1600° and 1700° F. and found this same type of pearlite to exist in practically all the specimens.

It is quite possible that the specimen of which we have shown photomicrographs and which hardened normally for us, hardened because we used a slightly higher temperature and the divorced pearlite therefore had a greater and better chance to go into solution than in all the cases mentioned by McQuaid and Ehn.

We presume the authors are investigating further and we can expect to learn from them just what oxides and how much must be present in a melt to give these results. Also, might not other conditions in the melting and working cause the same trouble.

HENRY S. RAWDON,* Washington, D. C. (written discussion).—The writer does not wish to imply in this discussion that he underestimates

* Physicist, Bureau of Standards.

or belittles the practical importance of the investigation; the lack of specific details concerning the materials used, however, is to be regretted. By reference to well-established and accepted facts concerning the structure of steels, at least some of the phenomena observed by the authors can be explained as satisfactorily as by reference to the rather mysterious condition designated as "the presence of excess dissolved oxide," the assumption of course being that all other possible causes incidental to the carburizing process itself have been eliminated. It is quite generally conceded by metallographists that the greater part of the oxide in steel, such as results from the deoxidation process, if it persists in the metal, exists as discrete particles of such a size as to be readily observable under the microscope rather than in the form of solid solution in the iron matrix, that is dissolved. The recent investigations by Stead and by Whiteley[11] indicate a very limited solubility for oxide in iron or steel. The total percentage of oxygen present in steel is always very small. Camp[12] states that even overblown bessemer steel contains less than 0.15 per cent. Shimer and Kichline[13] were unable to put more than 0.075 per cent. oxygen into steel even by the most drastic attempts to oxidize it; finished steel, they claim, contains no more than 0.03 per cent. of oxygen. The results obtained by the Bureau of Standards in the analysis of numerous specimens of steels prepared under different commercial conditions used in the study of the determination of oxygen in steel fully confirms this[14] and indicate, in general, a somewhat lower oxygen content. In order for the oxide to be responsible for the structural features noted by the authors in the steels after carburization, it would be necessary that this oxide remain *in situ* unaffected by any of the chemical changes that occur during the process of carburization, as it is during the cooling of the specimen after the carburization process has been largely, if not entirely, completed that the cementite assumes its abnormal state. The writer believes that the nature of the cementation process renders this fundamental assumption difficult, if not impossible, to maintain when the low percentage of oxide present and the active conditions tending toward its removal during the carburization process are considered.

It is quite generally admitted that, except in a few special cases, carbon enters steel during the process of cementation as one of its gaseous compounds, carbon monoxide being the most active in the ordinary

[11] J. E. Stead: Solid Solution of Oxygen in Iron. *Jnl.* Iron and Steel Inst. (1921) **103**, 271. J. H. Whiteley: Cupric Etching Effects Produced by Phosphorus and Oxygen in Iron. *Ibid.*, 277.

[12] J. M. Camp and C. B. Francis: "The Making, Shaping and Treating of Steel," 568. Pittsburgh, Pa., 1920, Carnegie Steel Co.

[13] Over-oxidation of Steel. *Trans.* (1913) **47**, 436.

[14] Bureau of Standards *Sci. Paper* 346 and *Tech. Paper* 118.

process of carburization.[15] This gas penetrates the hot metal and reacts with the iron according to the equation:

$$2CO + 3Fe \rightleftarrows Fe_3C + CO_2$$

The cementite formed dissolves in the iron to form austenite, the carbon dioxide gradually diffuses toward a zone of lower concentration of this gas, that is outward from the specimen. In the presence of an excess of CO_2, it might be expected that the reverse of the reaction given would occur, thus resulting in decarburization; however, the constant influx of carbon monoxide renders the probability for this very slight.

It is to be expected that oxides present in the steel, for instance FeO, will be acted upon by the carbon monoxide in a manner similar to that described for iron. In this case, an equation representative of an intermediate reaction stage, such as occurs in the reduction of iron ore in the blast furnace, may be written:

$$FeO + CO = CO_2 + Fe$$

It would appear, then, that iron oxide, which is well recognized as one of the most detrimental oxides possible on the properties of the metal, would not survive the chemical reactions that constitute the process of cementation.

Fig. 11 shows plainly that the unsatisfactory or abnormal steel had a pronounced tendency to develop a banded or fibered structure upon heating. There is considerable uncertainty as to the exact nature of this structural defect. Oberhoffer has shown that it may occur in certain steels merely as a result of the heating they receive and in its initial state the steel may show no pronounced evidence of it when examined by ordinary methods.[16] Although it has been suggested that the distribution of oxides in steel is related to banded structure and ghost lines, these structural features are more generally considered to be much more closely related to phosphorus distribution. Portevin[17] has shown that to wipe out the banded appearance caused by the non-uniform distribution of phosphorus, annealing for 6 days at 850°–900° C. was necessary.

The cupric reagent generally used for revealing the distribution of phosphorus is difficult to use, particularly for material that varies as much in its composition as a steel after case carburization. The failure of the authors to obtain convincing results with this reagent after cementation, hence their conclusion that 24 hr. heating at the carburizing

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[15] E. E. Thum: The Cementation of Iron and Steel. *Chem. & Met. Eng.* (1917) **16**, 385. This article is an admirable condensation of Giolitti's reference book, "The Cementation of Iron and Steel."

[16] Oberhoffer: *Zeit. Anorg. Chemie* (1913) **81**, 156.

[17] Portevin and Bernard: *Rev. de Mét., Memoirs* (1918) **15**, 273.

temperature was sufficient to permit thorough diffusion of the phosphorus, may have been due to this cause. However, the observation that the ghost lines persisted in the metal seems rather contradictory.

The effect of phosphorus on the precipitation of cementite and the formation of ghosts has been discussed by Hoyt[18] and the effect produced is in line with the observations of the authors. The general restraining effect of phosphorus on the carburization of iron might be expected to cause the depth of the case on the abnormal steel to be somewhat less than on the normal. However, under the conditions that obtain during the cementation process, when the metal is exposed to a constantly renewed supply of carbon monoxide, it is not surprising that the chemical analyses showed little difference. However, Figs. 1 and 2 suggest a noticeable difference in the depth of the case produced on the two steels.

Although a general chemical analysis may have shown that the average phosphorus content of the steel described was not abnormal, too much should not be argued from the results. It is well known that a general analysis tells little, if anything, concerning the distribution of the elements within any specimen analyzed and the phosphorus content of certain streaks in a steel sample is often many times that of the average for the piece. It is the effect of these "micro segregations" that the writer wishes to emphasize.

Another element that may have an effect on the form and manner in which cementite is precipitated from austenitic solution is manganese, although usually the effect is not so pronounced as that of phosphorus. The writer does not agree with the authors' conclusions and explanation of their observations. The effect of manganese on the structure of carbon steels has been summarized by Howe[19] as a "retarding action upon the transformation and coalescence of micro-constituents into progressively coarser masses." Babochine[20] has shown that on slowly cooling very mild steel (0.2 per cent. carbon) the presence of 0.6 per cent. manganese was sufficient to prevent the formation of free cementite. Steels of lower manganese content showed free cementite when cooled slowly enough. It is generally recognized that the excess of manganese over the amount required for deoxidation and desulfurization enters into chemical union and strengthens the material. A forthcoming paper of the Bureau of Standards deals with this subject in detail. Most metallographists have accepted the explanation advanced years ago, which is discussed by Howe in the reference given, that the excess manganese remains in the steel as a constituent of a double carbide. The structure

[18] S. L. Hoyt: "Metallography," Pt. 2, 278. New York, 1920. McGraw-Hill Book Co.

[19] H. M. Howe: Rôle of Manganese in Steel. A. S. T. M. *Proc.* (1917) **17**, 5.

[20] A. L. Babochine: *Rev. de Mét.* (1917) **14**, 81; *Rev. Soc. Russe Metall.* (1915) **8**, 561.

of an annealed medium-carbon steel containing considerable manganese, *e.g.*, 0.75 to 0.80 per cent., shows that the relative amounts of ferrite and pearlite are quite different from those observed in a steel of the same carbon content with lower manganese. In fact, one may be greatly misled in the planometric method for determining carbon content if no consideration is given to the amount of manganese present.[21]

The writer believes that the results observed by the authors concerning the behavior of steels of different manganese contents are only manifestations of this characteristic influence of manganese upon the physical state of the pearlite. In this connection some photomicrographs published by Stenger[22] in the report of an investigation of the exfoliation of case-hardened steels are of interest. Two of the materials studied were low-carbon steels (approximately 0.15 per cent. carbon), which differed in their manganese content; though it is not stated that this difference was intentional. Specimen A (manganese 0.89 per cent.) after carburizing showed a case practically identical with that designated as normal by the authors; specimen B (manganese 0.54 per cent.) showed a case distinctly abnormal. The effect of the higher manganese content of specimen A, in retarding the coalescence of the micro-constituents so that grains of sorbitic pearlite uniformly surrounded by thin envelopes of ferrite resulted, while in the material of lower manganese content considerable coalescence occurred and a broken and "ragged" condition of the grains resulted, seems to the writer the most obvious explanation for the observed difference in behavior, that is so far as one can judge from the published evidence. It is also interesting to note that specimen B (the abnormal one) had been refined in the electric furnace. The results of some of the auxiliary experiments carried out by the authors to substantiate their hypothesis may be explained in an entirely different manner in the light of what has been given above. No allowance was made by the authors for any composition changes other than a possible change in oxygen content. The blowing of oxygen upon the surface of molten steel would not only oxidize the metal but would materially change the composition by burning out the manganese, carbon, and possibly other metalloids. Likewise in the fusion of steel by the fusion-welding process, the composition is changed, but to an even greater degree. The fact that some heats of steel taken from the electric furnace immediately after melting were found to behave normally during carburization appears good evidence to the writer that some consideration must be given to the composition of the steel scrap used in such experiments.

Nothing has been given by the authors, other than the deoxidizer used, by which the steels received from Professor Boylston could be identified in the published account of Boylston's work.[23] Presumably

[21] Burgess, Crowe, and Rawdon: *Trans.* (1913 **47**), 605.

[22] *Chem. & Met. Eng.* (1917) **16**, 425.

[23] *Carnegie Schol. Mem.*, Iron and Steel Inst. (1916) **7**.

they were from the series of experiment 2, in which case a steel of 0.37 per cent. carbon and 0.51 per cent. manganese was used for deoxidation experiments, rather than from experiment 1 in which the raw converter metal was simply treated with the proper deoxidizer but not recarburized. The steels of Boylston's experiment 2 have been analyzed by the Bureau of Standards for oxygen content and the results obtained have been published.[24] Each of the steels showed an oxygen content, as determined by the Ledebur method, considerably less than the average for commercial steels. The oxygen content ranged from 0.009 to 0.018 per cent., the average for thirteen specimens being 0.014 per cent. It does not seem probable that the results obtained by the authors in the carburization of these steels should be caused by variations in the oxide content. These steels were prepared under conditions that differed considerably from commercial practice so that any attempted explanation of their behavior would be more or less conjecture.

The writer has mentioned some conditions that should be considered in any attempted explanation of the phenomena described by the authors. The suggestions are not offered, however, as a full or complete explanation in any sense. In conclusion, the writer wishes to state that he fully agrees with the authors that anything which favors the coalescing of the cementite of the case into the spherodized condition during the process of cementation interferes to a marked extent with the results desired in the necessary subsequent heat-treatment of the carburized steel.

J. S. VANICK, Washington, D. C. (written discussion).—The necessity of studying steel making in an effort to overcome some of the difficulties mentioned must be apparent. It is furthermore quite evident that the ordinary specifications for the chemical composition of steels for case-hardening purposes do not protect the case-hardened part from difficulties beyond the control of the carburizing process.

The authors show that the progress of cementation is not affected but suggest that oxygen and its compounds may be dissolved in steel in sufficient quantities to interfere with the efficacy of the case-hardening process. The suggestion regarding the presence of oxygen in solution, I prefer to accept, although it is well to keep in mind the similar effects produced by banded segregations of other elements.

In the nitrogenization of low-carbon steel by the action of ammonia gas at low temperatures (300° C.), numerous instances were noticed in hardened steel in which the pearlitic patches of nitride were collected about the ferrite areas. These areas were considered to possess oxygen in solution because of the presence within them of slag or oxide particles or, more frequently, the severe coring or pitting of the areas when solid particles were absent. The pitting strongly suggested the ebulition of

[24] Bureau of Standards *Sci. Paper* 346.

gas while the metal was in the solidifying stage. The areas were considered important from the standpoint of their resistance to nitrogenizing gases, and the slightly greater resistance they offered was attributed to the change in rate that the nitrogenizing reaction experienced on encountering them.

That conditions similar to this exist in the steel described by the authors seems evident, and although the carburization was carried out at much higher temperatures the conditions are quite parallel. Some recent work on the relations between iron, carbon and oxygen has been done by Matsubara[25] whose work is an expansion of that of Schenk and Giolitti and their assistants, and is of fundamental importance in considering the problems of case hardening. From this $t - x$ diagram, Fig. 5, we find that at 950° C. (the approximate temperature at which the authors carry out their work), that the reaction

$$3Fe + 2CO = Fe_3C + CO_2 \qquad (1)$$

may proceed at a pressure of 1 atmosphere and a gas concentration of 7 per cent. CO_2. With an increase in CO_2 to 10 per cent. the reaction

$$3FeO + 5CO = Fe_3C + 4CO_2 \qquad (2)$$

may proceed. The reactions for carburization at 950° C. at a pressure of 1 atmosphere require for their consummation the presence of approximately 7 to 10 per cent. CO_2. The most significant feature of these equilibria is that an increase in the concentration of CO_2 permits the carburization of FeO to Fe_3C or cementite. Perhaps of equal importance is the position of the equilibrium line between FeO and CO, according to the equation

$$FeO + CO = Fe + CO_2 \qquad (3)$$

At 950° C. and 1 atmosphere, this reaction required 68 per cent. CO_2, or less, for its progress. Should the concentration of CO_2 increase until it exceeded the low figure of 68 per cent., it is evident, from the diagram, that the reaction would reverse and oxidation of the iron would begin. It is most important to note that the reactions marking the reduction of FeO by CO and the carburization of FeO to Fe_3C occur at lower concentrations of CO than the reactions showing the carburization of Fe. Why, then, should the presence of oxygen in a solid solution, which might be arbitrarily assumed to consist of Fe_xFeO_y, interfere with the thorough distribution of carbon?

The solution to this question lies in the difference in the rate at which the cited reactions progress. It is known that 10 to 20 hr. are necessary to establish equilibrium in reactions such as these and frequently more time is necessary, even though special efforts are made to promote the attainment of equilibrium.

[25] Chemical Equilibrium Between Iron, Carbon and Oxygen. See page 3.

In the case of a low-carbon, case-hardening steel, the progress of diffusion would be limited to the rate at which the carburized zones are able to expel the CO_2 generated in accordance with reaction (1). If we may consider the solid solution Fe_xFeO_y to consist of unit lattices composed of atoms of Fe and O bound into a chemically homogeneous mass by interatomic forces, yet separated by interatomic spaces so that each lattice unit represents a cell or reaction chamber, the progress of the carburization into the oxygen-bearing zones may be more readily visualized. In the confined spaces of the interatomic reaction chambers, reaction (1) would be appreciably favored by the reduction, in volume, that the entering CO experiences on coming in contact with a large amount of Fe. The volume reduction would permit the infiltration of fresh quantities of CO thus allowing a more rapid cementation of Fe by the more rapid circulation and diffusion of CO.

For a solid solution Fe_xFeO_y containing a small amount of oxygen in solution, the progress of carburization would be severely retarded, principally on account of the generation of greater quantities of CO_2 at the outer edges of the FeO-bearing areas. The generation of a greater amount of CO_2 in accordance with reaction 2, with but a slight decrease in volume of the entering gases, would retard the speed of the reaction and increase the resistance to penetration and circulation of that part of the advancing CO that was able to reach the interatomic reaction chambers.

With a further increase in the percentage of CO_2 prevailing in the interatomic spaces, only reaction 3 could proceed. This reaction is not accompanied by a change in the volume of the reacting gases, hence no special inducement would be offered for the CO to replace or dilute the CO_2 that is present. The last-mentioned condition is probably not obtained, because the structure of the metal, as illustrated by the authors, shows the presence of cementite in close contact with the (Fe_xFeO_y) solid solution. Apparently the amount of FeO present is so small that carburization remains within the limits set by reaction 2 and the diffusion and circulation of CO_2 in the interatomic chambers is just enough to provide for the gradual progress of this reaction. This limit on the progress of the reaction agrees with the condition of the structure as described by the authors.

In heat treating, the failure of the cementite formed in the carburization of the metal to diffuse thoroughly into the oxygen-bearing zones is quite possibly due to the pressure that is revived in keeping with reaction 2 when the temperature is raised to that customarily used in hardening. The small amount of cementite diffusion that does occur would create a sharp composition gradient within which, after quenching, the zone of variable martensite and deep variable troostite described by the authors might be expected to occur.

At another point, the authors suggest that the cause of soft spots in high-carbon steel may be the presence of oxygen-bearing areas. While admitting the possibility of soft spots in high-carbon steels caused by the presence of oxygen in solution, the probability of such an occurrence is exceedingly small. In the manufacture of high-carbon steel, an excess of carbon would be present in the liquid solution and the rapidity with which it would react with an Fe_xFeO_y solution at the high temperature of the liquid would provide for a rapid decomposition of the FeO and the rapid assimilation and distribution of carbon. Obviously the conditions attending the introduction of carbon into tool steel and case-hardened steel are so widely different as to be beyond comparison. As the manufacture of high-carbon steel requires a large amount of carbon in a liquid solution and the reactions in the liquid are much more rapid and complete, we must look toward other sources as the probable causes of soft spots in these steels.

H. W. McQuaid and E. W. Ehn (authors' reply to discussion).—This paper was written some time before the theoretical questions involved had been sufficiently studied, so that many of the objections would probably not have been presented if later experiences and conclusions had been included. It is not easy to give a satisfactory theoretical explanation to all phenomena observed, but this has been tried by one of the authors in a paper presented at the May, 1922, meeting of the British Iron and Steel Institute.

The theory rests on the assumption of the presence in the steel of minute ultra-microscopic solid particles of oxides probably, but not necessarily, held in colloidal solid solution. In a liquid steel, with a large number of particles of this kind, the solidification of the steel in the ingot will simultaneously start at a large number of points, giving a fine-grained abnormal steel. Experiments have shown that when a steel containing much gas is deoxidized by aluminum immediately before tapping, this effect is very pronounced, which agrees with the results obtained with Doctor Boylston's test pieces (Figs. 43 and 44). In this particular instance, Al_2O_3 is undoubtedly the active body, but there is every reason to assume that in other circumstances other oxides will act in a similar manner.

When the steel is clean and well deoxidized, these starting points for the crystallization in the ingot are few, and the crystals will grow large and be well developed; *i.e.*, giving large sharp-cornered grains such as are present in normal steel. These properties are not changed by the different operations in the conversion of the steel;[26] and by germination effect, Jeffries and Archer[27] have given a very satisfactory explanation for

[26] Compare Giollitti "Heat-treatment of Soft and Medium Steels," translated into English by Thum and Vernaci, 13 and 14.

all phenomena connected with the grain size of the different steels. This is also true of the disintegration of the pearlite in the hypereutectoid zone of very abnormal steels. The phenomena encountered in hardening obtain an equally satisfactory explanation.

The authors believe that even if each of the experiences given in the paper might not be convincing, together they form a satisfactory proof for the soundness of the above theory and their daily experiences in dealing with these problems strengthen their conviction. If a theoretical explanation, such as is outlined above, is accepted, it becomes quite evident that the oxygen content determined by, for instance, the Ledebur method will not be an indication of the properties of the steel.

Several of the persons taking part in the discussion emphasize the desirability of oxygen determinations, but an analysis of the oxygen content by means of, for instance, the Ledebur method, will mainly give the oxygen content of the occluded gases, which is of no account in regard to the structure and will probably not include the oxygen contained as oxides, as the reduction of the oxide particles will be difficult to obtain. An oxygen analysis by present methods is accordingly of no interest in this connection.

In regard to the discussion by French and Jordan, the authors do not wish to have a statement attributed to them that there is any essential difference in the nature of electric-furnace and open-hearth steel. It is true that, on the average, better results have been obtained with electric-furnace steel than with open-hearth, but many instances have been found where electric heats have been extremely abnormal and many open-hearth heats have been found to be of excellent quality. It depends entirely on the care that has been taken in the making of the different heats, especially in regard to the way the deoxidation of the steel has been made, and excellent clean steel may be obtained with either method.

As to the proper explanation of the phenomena described as normal and abnormal, the authors are well aware of the difficulties in obtaining definite proof for their theories, and have read with great interest the discussion by French and Jordan. They firmly believe that the proper explanation is to be found in improper deoxidation of the steel when made. The important feature of the authors' theory, however, is not that the oxygen content in the steel directly causes the abnormal properties, but that these properties are due to the presence in the steel of minute solid oxide particles, presumably in solid solution. Any kind of impurities will cause abnormal properties if they fulfill this condition and all evidences indicate that these impurities consist of oxides, but it is reasonable to assume that nitrides will cause the same phenomena under suit-

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[17] Grain Growth and Re-crystallization of Metals," *Chem. & Met. Eng.* (1922) **26**, 454.

able conditions. The small value of analysis of the gas content of the steel under these conditions is therefore apparent.

The experience with silico-manganese steel related by French and Jordan is similar to that obtained by Schmid, but the authors do not believe that this is necessarily proof that nitrogen is actually the active element, which fact French and Jordan also state. Future experiments of this kind should be accompanied by carburizing tests, so that the normal and abnormal properties will be brought out more clearly.

Schmid's corroboration of their experience is pleasing to the authors, especially as the steels are of a different character; it shows that carburizing tests are useful to solve problems in connection with special heat treatment of various steels. There is no doubt that non-metallic impurities finely dispersed through the steel have a decided influence on the way the steel responds to a hardening operation and other heat treatments, but it would be premature to discuss the results as more research work is necessary before the various results brought out in the discussion can be properly explained.

In answer to Professor White's remark about the steel subjected in molten condition to a stream of oxygen, the authors would state that the quality was checked and found entirely normal, but the photomicrograph was not included in the paper because of the necessity of restricting the number of illustrations. His experience with the influence of non-metallic inclusions, in general, check with that of the authors, who are willing to agree that any kind of solid impurities finely dispersed through the steel in proper concentration will cause abnormal properties. A large number of tests with different chemicals introduced into drilled holes in normal steel have proved this conclusively. As a possible reason for uniformly abnormal properties in commercial steels both sulfurous and phosphorous segregations are, however, out of question.

The discussion by Stagg and Spalding brings out some points concerning ghost lines that check closely with the experience of the authors in the same respect. Figs. 50 to 57 show exactly the same characteristics as the Figs. 25 to 28, and that the appearance is not exactly the same depends entirely on the choice of magnification and the spot to be photographed. Ghost lines showing all degrees of disintegration of the pearlite, from complete to hardly visible, have been observed, as well as many cases of exactly the same appearance as those shown by Stagg and Spalding.

In regard to the hardening of the specific steel mentioned in their discussion, the result is not unexpected. That no soft spots were obtained and that the ghosts showed a normal martensitic structure after the quench is entirely feasible and checks with our experience. It must be remembered that in hardening abnormal steel, usually, only spots become soft; the greater part of the surface is hard; this apparently is caused by the unevenness in the quench. The authors are aware that

a high hardening temperature is beneficial for obtaining a martensitic structure, and the practice of using a raised hardening temperature has been successfully employed by them for years for parts that consist of more or less abnormal steel. The contention that this should be due to the greater ease with which the cementite is dissolved, however, is not correct; with respect to this the authors refer to a paper by Portevin and Garvin.[28] It has been repeatedly verified by laboratory experiments, with gradually raised hardening temperature, that there is no difficulty whatever, even in the most abnormal types of carburized steel, to obtain the cementite in solution and it is in the following quench that the soft spots develop, because an abnormal steel needs a much faster quench than a normal steel in order to form martensite. The troostite obtained in the quench is bulky and entirely different in nature from that obtained by drawing back an already hardened steel. A more detailed discussion of this question is given in the paper presented before the British Iron and Steel Institute in May, 1922.

Mr. Rawdon's statement that it is necessary that the oxide particles be unaffected by the carburizing gases in order to affect materially the carburizing qualities of steel is undoubtedly right. It is difficult, however, even with hydrogen as the deoxidation reagent, to obtain a complete deoxidation; and in an oxygen determination, very thin chips, long time, and high temperature are required. With CO as the deoxidizing reagent, even more difficulty will be experienced. Moreover, SiO_2, Al_2O_3, or TiO_2 will not be affected and in the carburizing the possible reduction of the FeO particles by CO gas would take place simultaneously with the chemical reaction of carbon absorbtion from the CO by the γ iron. So it becomes a question of the degree of affinity of the γ iron and the oxide particles for the excess carbon in the CO gas, whether one reaction or the other will take place. The authors have, in a few specimens, observed how a typical abnormal structure, as far as the core is concerned, has been changed into a normal structure in the case. This indicates that a reduction of the oxides had taken place and gives added interest to Mr. Rawdon's statement. Just what conditions control this reaction is, however, difficult to ascertain as a number of factors enter into it.

The opinion that phosphorus rather than oxides is responsible for ghost lines in steel was general until a few years ago. Portevin, McCance, and Whiteley, during the last two or three years, have proved that the main reason for ghost lines is oxygen.

That phosphorus present as segregations can cause abnormal spots, just as any other impurity present in minute particles and in proper concentration, has been proved by laboratory experiments with different kinds of artificial inclusions. That a phosphorus content of, say, 0.020

[28] "Influence of the Rate of Cooling in Hardening of Carbon Steels," *Jnl.* Iron and Steel Institute (1919) No. 1.

per cent. could cause a uniformly abnormal structure through a 50-ton heat without traces of ghost lines or other segregations is quite impossible. If the structure were dependent on the phosphorus content, the structure should have some connection with the phosphorus content obtained by analysis, but such a correspondence has not been observed. In the early stage of this investigation, because of this possibility, this point was watched closely, when it was found that an abnormal structure is just as likely to be found in a steel with 0.015 per cent. phosphorus as in a steel with 0.040 per cent., *i.e.*, the extreme limits for the steels in our practice.

In regard to the possibilities of manganese as the cause of abnormal carburizing qualities, though hundreds of heats were checked for manganese content, no direct relationship between the structure and the manganese content is found. The manganese content in this steel varies from 0.35 to 0.65 per cent., usually being between 0.50 and 0.60 per cent., but heats of steel at both extreme limits of manganese content were perfectly normal as well as abnormal. That a low manganese content often is accompanied by abnormal carburizing properties is true, but this is a sign of a generally poor heat and the abnormal properties cannot be considered as being caused by the low manganese content. This does not mean that manganese is without influence in the case mentioned by Rawdon, but the manganese content there is much higher. In the case of the steel used by the writers, the small variation in manganese content cannot possibly, either alone or in conjunction with phosphorus, be responsible for the variation in carburizing qualities.

The authors admit that a change takes place in the composition of the steel when welded and when oyxgen is blown into molten steel; this was checked by analysis at every stage of these experiments. But they are not inclined to regard this change as the cause of the abnormal properties although the possibility of an influence is admitted.

The writers note with satisfaction that Mr. Rawdon offers no objection against those experiments which might be regarded as the strongest proof in favor of the theory of ox ides as responsible for abnormal properties in steel. Fig. 36 shows the hypereutectoid zone of a burnt and carburized specimen taken from the same bar as the sample shown in Fig. 1. The phosphorus or manganese content in this specimen certainly cannot be changed by burning, and the writers do not believe it possible to explain the change in properties in any other way than by absorption of oxygen. By burning the end of a bar in a forge fire, followed by carburizing, and the preparation of a lengthwise section, the change in carburizing qualities can be gradually followed. Mr. Rawdon's theory also fails to explain how an inclusion of mill scale, such as is shown in Figs. 37 and 38, can produce an abnormal structure, a phenomenon that is observed quite frequently.

The authors admit that it might have been desirable to give more details of the results obtained with Doctor Boylston's specimens, although the results were included more as an interesting experience than as a proof for the value of different deoxidizers, as many more experiments of this kind are necessary. The steel samples referred to were taken from Boylston's experiment No. 2 and the samples received were from ingots No. 1, 5, 8, 11 and 14. That the oxygen content, as determined by the Ledebur method, shows little variation, does not affect the possibility of oxide as causing the abnormal properties of some of the steels. The deoxidizers are likely to combine with the oxygeniferous gases in the molten steel, forming oxides, and if these oxides are of such a nature that they have a tendency to become suspended in minute particles in the steel, they will cause abnormal carburizing properties. If, on the other hand, they coagulate into larger bodies or are entirely removed from the steel, a steel of good normal properties will be obtained. This theory checks very closely with the germination theory of crystallization published recently by Jeffries and Archer.[29]

Mr. Vanick's analysis of the carburizing process has been read with much interest, but the authors cannot agree with several of his conclusions. His contention seems to be that the oxides in the steel participate in the chemical processes during the carburizing of the steel, whereas the authors, except for the rare cases mentioned in answer to Mr. Rawdon's discussion, believe that no such participation takes place. It is true that the depth of penetration is affected, but except for this fact there is no interference from the oxides with the thorough distribution of carbon during the carburizing. It is commonly recognized that in a specimen, during the carburizing, the carbon content decreases uniformly from a maximum at the surface to a minimum, corresponding to the carbon content of the core. Any irregularities in the distribution of carbon is thus of secondary nature obtained during the cooling of the specimens, and the use of equilibrium diagrams and equations, corresponding to 950° C., is not justified.

The theoretical analysis of the influence of different amounts of CO and CO_2 in the carburizing gases is interesting, but does not correspond to actual conditions in a commercial carburizing with commonly used compounds. The gases that are given off by most carburizing compounds at 950° C. have an approximate analysis of:

CO_2	0 to 2 per cent.
CO	40 to 50 per cent.
H	30 to 50 per cent.
CH_4, C_2H_2, N	5 to 10 per cent.

[29] *Loc. cit.*

A gaseous mixture of this kind is not likely to follow the same laws as a mixture of only CO and CO_2; this is said with full appreciation of the fact that for theoretical investigation the principle of considering only the CO and CO_2 content must be considered as correct. There is also no doubt that the CO_2 content in the inter-atomic chambers in the surface of specimens being carburized is considerably higher and the analysis of the conditions during the carburizing, given by Vanick, the authors accept.

Mill scale on the surface of carburized specimens always is reduced to iron and after carburizing shows an abnormal structure of comparatively high carbon content, but mill-scale inclusions in the steel, although they materially influence the structure of the surrounding steel, never are reduced. This reduction is caused by the hydrogen rather than by the CO, as it is unlikely that the CO_2 content is as high as 7 per cent., which according to Vanick is necessary for the reduction of FeO.

His remarks concerning the occurrence of soft spots in hardening are due to a misunderstanding of the phenomena described. That soft spots should correspond to oxygen-bearing areas is not correct and this misunderstanding is apparently also the reason for his remarks in regard to the possibility of soft spots due to non-metallic impurities in hardened tool steels.

Surface Changes of Carbon Steels Heated in Vacuo

By E. Heaton Hemingway,* Ph. D., and George R. Ensminger,† Watertown, Mass.

(Lake Superior Meeting, August, 1920)

During the past year, the Watertown Arsenal has been interested in the occluded gas and oxide content of certain ordnance steels in order to determine, if possible, whether some of the peculiar failures in their physical properties might not be traced to these causes. For the purpose of best accomplishing a study of this nature, it was decided to heat the various samples of steel in a vacuum for definite periods of time at high temperatures and carefully examine the quantity and composition of the gases evolved. By the use of a fused quartz tube fitted with a water-cooled, ground-glass stopper, it was possible to maintain a vacuum at a temperature of 1000° C. for 10 hr. without perceptible leakage being evidenced as measured by a McLeod gage.

The silica tube was connected with an evacuating system so constructed that the volatilized gases could be removed from time to time and a low vacuum of 0.0002 to 0.0010 mm. of mercury continuously maintained. At no time during the period of heating or in the removal of the gases did the evacuated system come in contact with rubber stoppers or any rubber connections, making contamination from such a source impossible. In other words, the only volatile products that could be obtained must necessarily have come from the steel itself or from the glass and fused quartz system or from the mercury used as a sealing agent.

In the earlier experiments, the steel treated was in the form of turnings, but this practice was discarded because the weights of the turnings before and after being heated were widely inconsistent, even when taken from the same piece of steel. This discrepancy developed largely through variation in the amount of metal volatilized with the gases; this metal could always be seen in the form of a ring where it condensed in the cooler portion of the tube in either the amorphous or crystalline condition. Because of the frequency in occurrence and the variation in the manner of deposition, this material was roughly analyzed and found to consist for the most part of iron. At the same time two samples of steel that had been

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given several treatments in the vacuum were analyzed to determine whether any of the individual elements, commonly found in steel, were volatilized with the iron. The following analyses show that a loss in the carbon and manganese content took place in both instances, while a relatively large loss was recorded in the sulfur content of one sample:

	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Sulfur, Per Cent.	Phosphorus, Per Cent.
Original (1).....	0.45	0.79	0.23	0.056	0.045
Final (1).....	0.40	0.54	0.225	0.038	
Original (2).....	0.109	0.372	.....	0.030	
Final (2).....	0.075	0.330	.....	0.031	

After having made the above test, the volatilized products from several experiments, which had condensed on the tube, were collected in the form of their soluble salts and qualitatively analyzed. These analyses revealed that, in addition to the iron, an appreciable quantity of manganese and a trace of copper were present. No traces of either carbon or sulfur in the free or combined state were found and it is believed that the loss in these elements could be accounted for in the gaseous oxide products evolved, such as carbon monoxide and sulfur dioxide.

The surfaces of the turnings heated were always so silvery white in appearance that it was thought that mercury vapor might have condensed and formed a thin surface coating. However, the most careful analyses of the solutions obtained through the dissolving of the surfaces did not give the slightest trace of mercury.

Since the quantity of iron volatilized was much larger when the same weight of steel was heated in the form of turnings than when heated as a solid piece, it was thought that the volatilization might be proportional to the amount of surface exposed. It was, therefore, decided to use a cubic inch of steel as a sample in order to deal with the same amount of surface in every case. Although this tended to make the results more uniform, it was soon discovered that it would be difficult, if not impossible, to estimate the weight or amount of oxide and gas given off by the losses of weight incurred in heating these cubic samples. These samples of steel, also, after having been heated in the vacuum, showed mercury-like surfaces similar to those noted and previously described in the case of the turnings. In fact, these surfaces were brightened, even though they had been severely oxidized before being placed in the vacuum furnace. However, the quantity of the gas given off in such instances was materially increased, especially the carbon monoxide. This led to the

belief that the thin coatings of iron oxides reacted at 1000° C., or below, to give carbon monoxide and iron according to the following equations:

$$3Fe_3C + Fe_2O_3 = 3CO + 11\ Fe$$
$$Fe_3C + FeO = CO + 4\ Fe$$

It is quite evident that as long as there is any carbon present in a plain carbon steel, this carbon will tend to react with the iron oxide to give the volatile product, carbon monoxide, and pure iron. In fact, it should be possible to decarburize completely a piece of carbon steel by this method, provided there is sufficient oxide present and time is allowed for the completion of the reactions.

This point is of particular interest in that any segregated oxide located within the steel would be expected to behave in a similar manner; namely, react with the carbide to form free iron and carbon monoxide. The carbon monoxide, being a volatile gas, would leave the steel and pass into the evacuated tube. The amount of gas obtained then becomes a direct measure of the quantity of oxide contained in the steel. From the appearance on the surface of the samples, it is probable that the reaction of carbide and oxide proceeds to completion below 1000° C. and that it is unnecessary to heat the sample above this temperature, as has commonly been believed, in order to obtain all the oxide content in the form of a gaseous product.

From the foregoing observations, it became essential to remove all tarnished or oxidized coatings, since such surfaces would lead to erroneous results in the quantity and composition of gas evolved. For that reason, all specimens were highly polished and kept in desiccators until ready for use. It was on these surfaces that the peculiar polyhedral structure shown in Figs. 5 and 6 was observed.

Similar structures were observed and studied as early as 1909 by Rosenhain and Humfrey,[1] when they were working with a steel of 0.029 per cent. carbon content. The following year, Kroll,[2] in the study of the crystallography of the iron-carbon system, noted this same type of heat relief on medium- and low-carbon steels heated either in a vacuum or in an atmosphere of inert gases. In his work, he used these heat-relief boundaries as proof of the gamma and beta iron theory and, by slightly oxidizing his samples at certain definite temperatures, stated that he had evidence of the existence of martensite. Later Humfrey[3] in his work on the intercrystalline fracture of iron and steel, made the following observations on polished samples of electrolytic iron after vacuum heating at 1000° C. and allowing to cool under the same conditions:

[1] *Proc.* Royal Soc. Lond. (1909) **A 83**, 200.
[2] *Jnl.* Iron and Steel Inst. (1910) **81**, 304–402.
[3] Iron and Steel Inst., *Carnegie Memoirs* (1912), **4**, 80.

A deeply marked network of polyhedral crystals with frequent parallel twinning which probably represents the outlines of the gamma iron existing above 890° C.

A second and larger network of crystals the boundaries of which cross those of the first at random, which could be revealed after straining or etching and were the final alpha crystals.

At that time he did not develop, in detail, any reason for this peculiar surface relief other than the fact that the alpha and beta crystals, which are of the same conformation have resulted from the recrystallization of the gamma crystals, the outlines of which were still discernible. He left the theoretical discussion to be taken up by Rosenhain and Ewen,[4] who attributed this crystalline structure to either or both of the following causes:

That the amorphous metal which lies in the grain boundaries has a higher vapor pressure than the crystalline material and has evaporated faster causing a heat relief and intercrystalline brittleness.

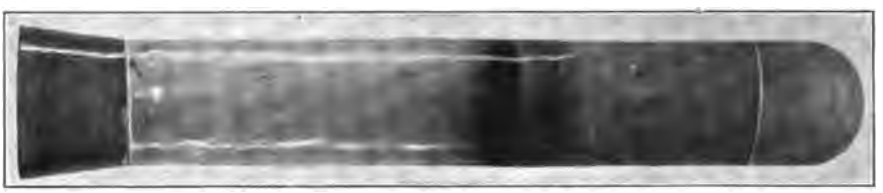


FIG. 1.—VACUUM TUBE SHOWING RING OF METAL CONDENSED AT POINT WHERE TUBE WAS COOLED.

That the amorphous film of metal produced by the polishing of the specimens has rearranged on being heated.

In 1914, Ewen[5] drew the following conclusions:

That the expansion and contraction of the iron or steel from the beta to the gamma condition and reverse might account for surface reliefs.

That the volatilization of amorphous material would not alone explain it because of the very low loss of weight during a vacuum treatment.

That the structure developed below the beta range might be due either to selective volatilization or unequal expansion of the iron crystals in different directions.

Recently, H. S. Rawdon and H. Scott[6] have drawn similar conclusions; namely, that this structure is caused by a slight roughening due to volatilization and to a slight buckling of the surface due to the volume change accompanying the transformation. They further state that the surface metal rapidly loses its carbon content through the volatilization of the

[4] *Jnl.* Inst. Metals (1912) **8**, 149–185.

[5] *Int. Zeits. für Metallog.* (1914) **6**, 1–17.

[6] See page 414.

iron carbide, which reaction becomes especially marked at a temperature above the A_1 transformation.

From their observations, however, the authors of this paper are led to believe that this surface relief has resulted from both a volatilization and a redeposition of iron rather than from any of the many explanations offered. That there is sufficient iron volatilized to produce such an effect can be evidenced by the amount of material deposited in the cooler portions of the vacuum tube. The ring of deposited metal formed at the point where the tube has been water cooled is evident in Fig. 1.

As a further proof that relatively large quantities of iron were vaporized and redeposited during the vacuum treatment, a small piece of clean platinum foil was placed near, but not in contact with, some steel turnings and heated at 1000° C. for several hours, the vacuum being maintained constantly throughout the experiment. A portion of the platinum foil was buried in alundum sand and consequently was protected from the vapors of iron. That portion which was unprotected from the vapors was thickly covered with a layer of iron, which could plainly be seen with the naked eye. Figs. 2, 3, and 4 show this structure at ordinary and higher magnifications. The iron, which was later dissolved off and analyzed, built up and modified the crystalline structure that already existed in the platinum.

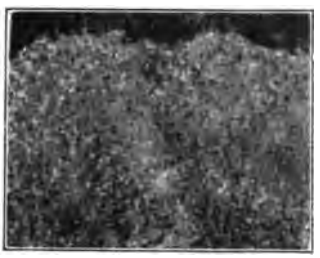


FIG. 2.—PLATINUM FOIL HEATED WITH STEEL TURNINGS, ENLARGED 1½ TIMES. CLEAR PORTION AT TOP WAS PROTECTED FROM IRON VAPORS.

To further develop this theory, it would be expected that iron or steel, held for any extended length of time at a temperature above the gamma range, would show a well-marked development of the gamma crystals. Not only will the vapor pressure be greatly raised, due to the higher temperatures, but one may logically believe that the vapor pressure of gamma iron will be much greater than that of the lower allotropic forms, since it is customary, as in the case of yellow and red phosphorus, that the allotrope which is stable at the higher temperature will have the higher vapor pressure. Hence the molecules, being much more free to move in this range, will vaporize more rapidly, but in time, providing the temperature is held constant, an equilibrium must be reached where the redeposition a must bear a fixed relation to the volatilization b; that is,

$$\frac{a}{b} = \text{constant value}$$

Both volatilization and redeposition should conform to the crystalline forces and would tend to develop the crystalline boundaries.

As the piece of iron or steel is gradually cooled through the A_3 point,

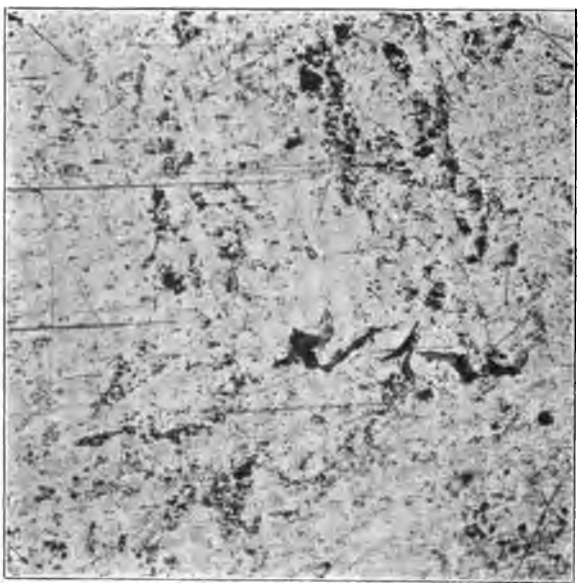


FIG. 3.—SURFACE OF PLATINUM THAT WAS PROTECTED FROM IRON VAPORS DURING VACUUM HEATING. SHOWS FINE POLYGONAL BOUNDARIES OF PLATINUM CRYSTALS. UNETCHED. ×50.

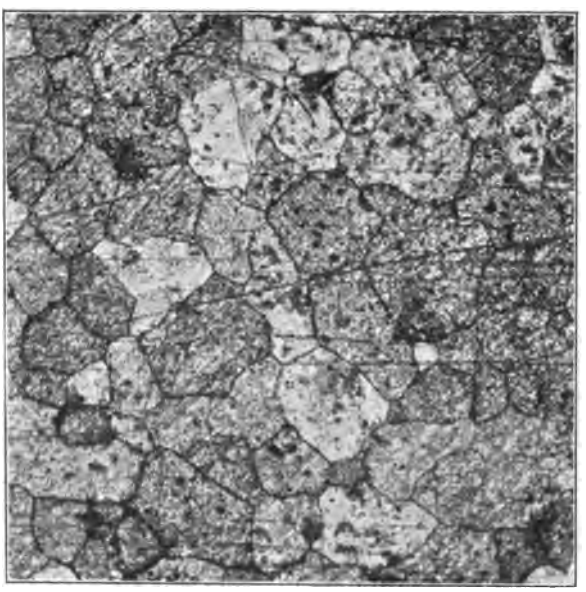


FIG. 4.—SURFACE OF PLATINUM ON WHICH IRON HAS DEPOSITED DURING VACUUM HEATING. UNETCHED. ×50.

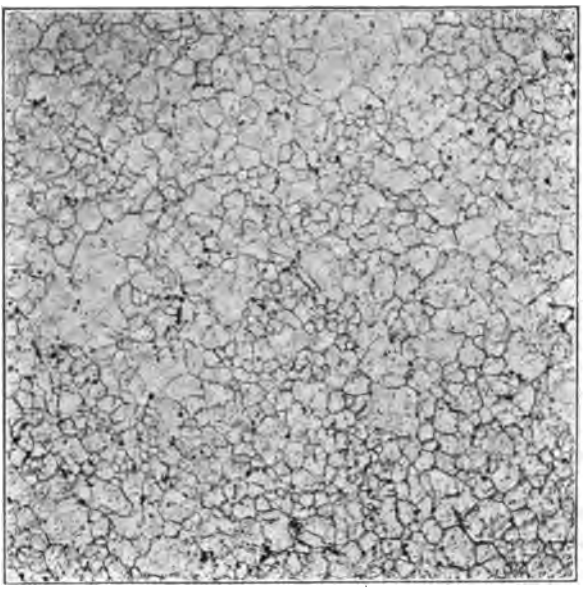


FIG. 5.—SURFACE OF LOW-CARBON STEEL UNETCHED AFTER BEING HEATED IN VACUO 6 HR. AT 1000° C. ×50.

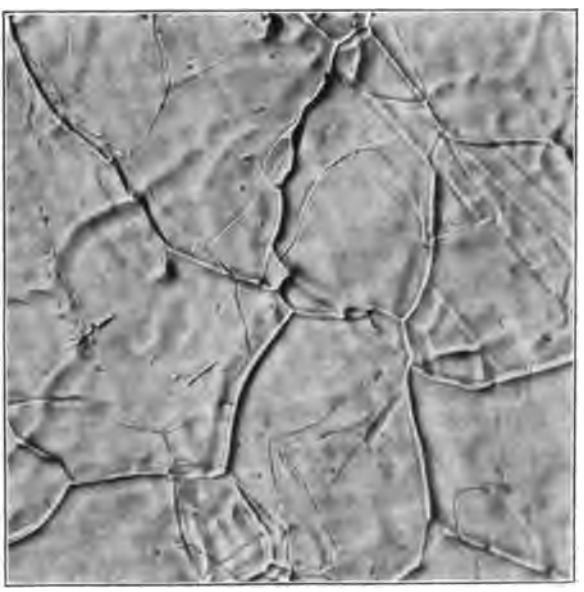


FIG. 6.—SAME AS FIG. 5, UNETCHED, SHOWING DEEP POLYGONAL GAMMA CRYSTALS CUT BY LIGHTER ALPHA BOUNDARIES. ×500.

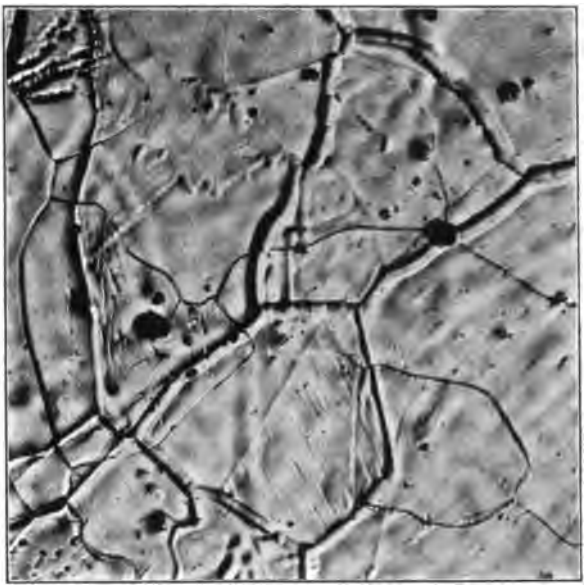


FIG. 7.—LOW-CARBON STEEL RELIEF SLIGHTLY ETCHED WITH 4 PER CENT. HNO_3, WHICH BRINGS OUT ALPHA STRUCTURE MORE CLEARLY. ×500.

FIG. 8.—LOW-CARBON STEEL, VACUUM TREATED, SLIGHTLY POLISHED ON ROUGE, ETCHED WITH 4 PER CENT. HNO_3, SHOWING ALPHA STRUCTURE WITH A FEW GAMMA MARKINGS REMAINING. ×50.

FIG. 9.—SAME AS FIG. 8. ×500.

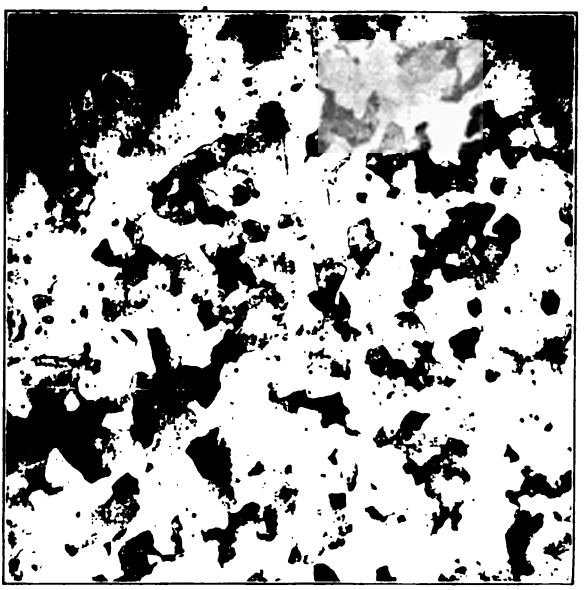


FIG. 10.—STRUCTURE OF LOW-CARBON STEEL ETCHED WITH 4 PER CENT. HNO_3, SHOWING EXISTENCE OF PEARLITE AND FERRITE AFTER RELIEF HAS BEEN POLISHED OFF. ×50.

FIG. 11.—SAME AS FIG. 10. ×500.

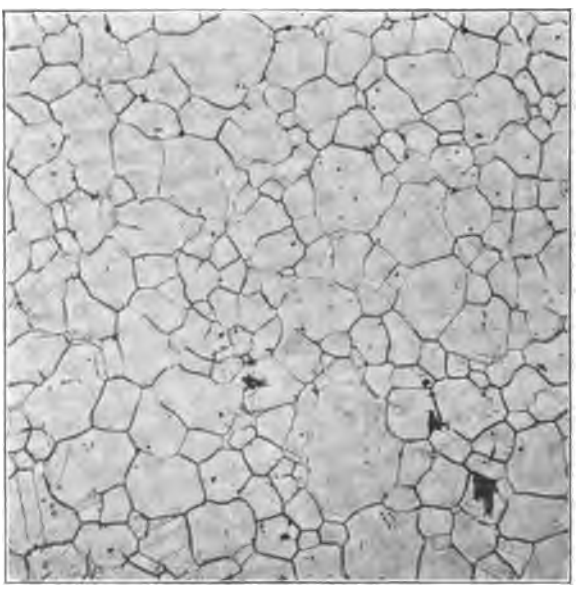


FIG. 12.—HIGH-CARBON STEEL UNETCHED; SHOWS POLYGONAL BOUNDARIES OF GAMMA IRON. ×50.

FIG. 13.—HIGH-CARBON STEEL UNETCHED SHOWING POLYGONAL STRUCTURE OF GAMMA IRON, RAGGED ALPHA IRON BOUNDARIES AND PEARLITE MARKINGS. ×500.

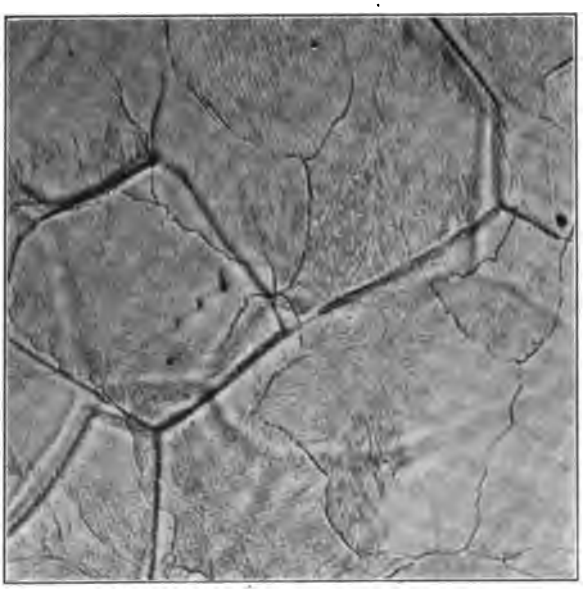


FIG. 14.—SAME AS FIG. 13, ETCHED WITH 4 PER CENT. HNO_3, SHOWING SHADOWED MARKINGS OF GAMMA BOUNDARIES THAT HAVE BEEN MERGED INTO LARGER FINAL GAMMA BOUNDARIES BY CRYSTALLINE GROWTH. ×500.

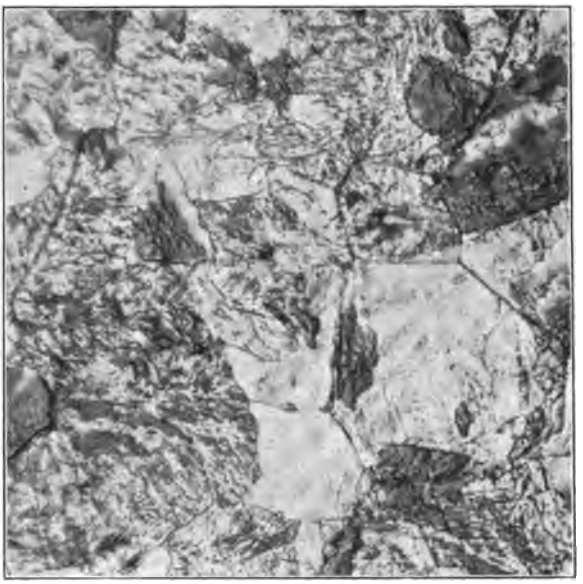


FIG. 15.—HIGH-CARBON STEEL SLIGHTLY ETCHED WITH 4 PER CENT. HNO_3 SHOWING PEARLITE BEGINNING TO APPEAR BUT FERRITE REMAINING ON SOME ALPHA CRYSTALS. ×500.

FIG. 16.—HIGH-CARBON STEEL WITH SURFACE ENTIRELY ETCHED OFF, SHOWING PEARLITIC ALPHA CRYSTALS WITH EXCESS CEMENTITE GATHERED IN OLD POLYGONAL GRAIN BOUNDARIES. ×500.

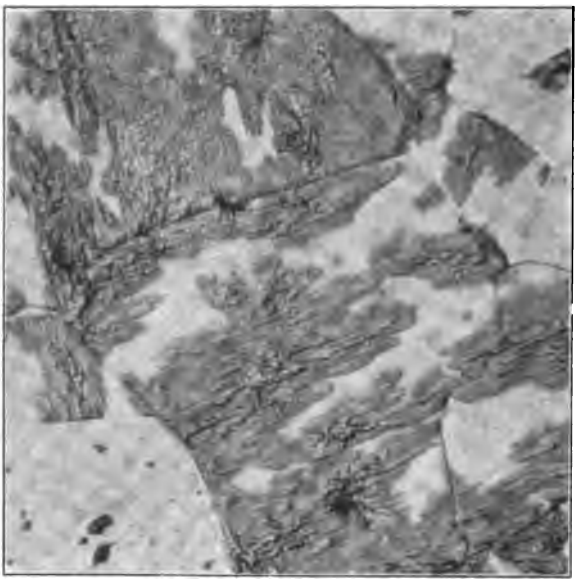


FIG. 17.—HIGH-CARBON STEEL, UNETCHED, SHOWING GRAY CRYSTALLINE DEPOSIT ON SURFACE. ×500.

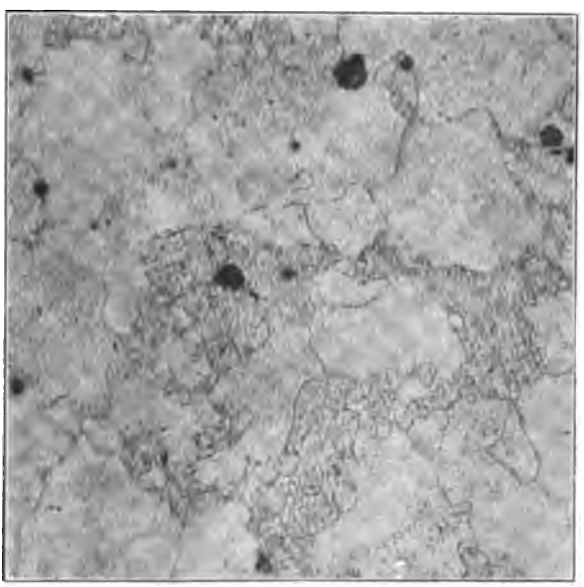


FIG. 18.—LOW-CARBON STEEL HELD 30 MIN. IN VACUO AT 760° C., UNETCHED, SHOWING LARGE FERRITE CRYSTALS AS WELL AS SMALL FERRITE CRYSTALS FORMING OVER PEARLITE. ×500.

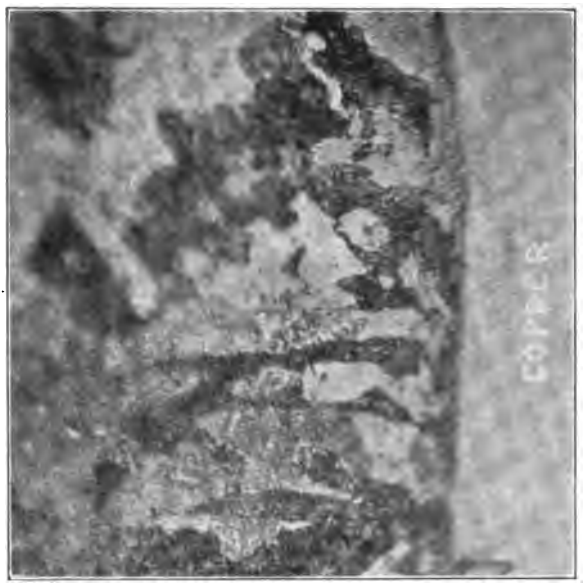


FIG. 19.—LOW-CARBON STEEL HELD 30 MIN. IN VACUO AT 760° C., COPPER-PLATED AND ETCHED WITH 4 PER CENT. HNO_3, SHOWING CROSS-SECTIONAL VIEW WITH PEARLITE EXTENDING PRACTICALLY TO THE SURFACE. ×500.

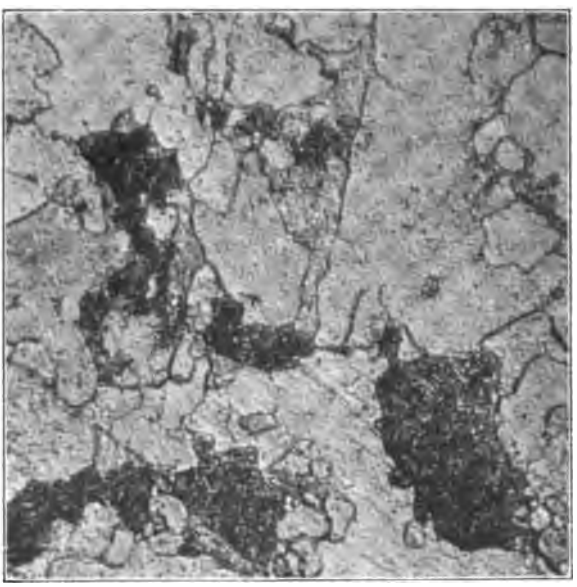


FIG. 20.—LOW-CARBON STEEL HEATED FOR 30 MIN. AT 740° C., ETCHED FOR 30 SEC. WITH 4 PER CENT. HNO_3, PEARLITIC CRYSTALS BEGINNING TO APPEAR. ×500.

its crystalline structure will change to that of the lower allotropes and the vaporization and deposition which must still continue, but at a slower rate, will tend to develop these new boundaries. On the other hand, if the sample is never taken above the A_3 point, only the crystalline boundaries of the lower allotropes can be developed.

Below the A_3 range, the vapor that condenses will build up a layer of pure iron of almost infinitesimal thickness, since carbides are no longer soluble in alpha and beta iron. In steels of higher carbon content, where the A_3 and A_2 points are gradually merged with the A_1 point, it is to be expected that the ferrite layer would be reduced in thickness. Taking as an example a steel of this composition, on being cooled from 1000° C., the iron vapors, when redeposited, will immediately dissolve in the solid solution until the temperature of the $A_{3,2,1}$ point is reached, where the vapor pressure will be so low that very little iron can be volatilized or redeposited unless held for an extended period just below this critical range.

Application to Low-carbon Steels

A steel containing 0.24 per cent. carbon, 0.61 per cent. manganese, 0.265 per cent. silicon, 0.053 per cent. sulfur, 0.031 per cent. phosphorus, when heated in vacuo for 6 hr. at 1000° C. and allowed to cool, developed a surface structure which conformed in every way with the above hypothesis. The gamma outlines are heavy and clear cut, as would be expected after holding the samples for such an extended period at this high temperature. Fig. 5 shows the structure at the lower magnification; Fig. 6 shows the gamma polygonal outlines much more clearly with twinning planes in four of the crystals.

The boundaries of the alpha crystals can be plainly seen at higher magnifications, cutting the gamma boundaries at various points without definite conformity. In fact, they appear to be actually superimposed on the deeper gamma boundaries in several places. There is also visible a third set of markings, very wide and more or less indistinct, which are of polygonal conformity and often show only two or three of their original boundaries. From their outline, the authors have decided that they originated in the gamma range and actually represent gamma boundaries which formerly existed, but have been enveloped in the later crystalline growth.

In order to justify the claim that the outer layer was composed of pure ferrite, the sample was etched for several seconds in 4 per cent. nitric acid. A pearlitic structure was not developed but the boundaries of the alpha crystals, which were formerly indistinct, were more deeply etched, as shown in Fig. 7. There can be no question that the alpha crystals are those with the sharp slender outline.

After this etching the sample was polished on the rouge and re-etched with 4 per cent. nitric acid. At lower magnifications (Fig. 8) the structure appears to be that of alpha iron but at higher magnifications (Fig. 9) some of the gamma outlines can still be seen. After a more severe polishing, it was again etched and the normal structure of the steel was revealed. Fig. 10 and 11 show the ferrite and pearlite grains. It is quite evident that the outer ferrite layer does not extend far below the surface of steel that has been treated in a vacuum at 1000° C. for this length of time.

Application to High-carbon Steels

When a similar treatment was applied to a steel containing carbon, 1.01 per cent.; manganese, 0.30 per cent.; silicon, 0.145 per cent.; sulfur, 0.023 per cent.; phosphorus, 0.046 per cent., reliefs similar to those shown in Figs. 12, 13, and 14 were obtained. Conforming with the theory developed in the first part of this paper, the gamma boundaries have become much more clearly defined since the gamma iron is now stable at much lower temperatures due to the merging of the A_1, A_2 and A_3 points. The ragged boundaries of the alpha crystals containing the pearlitic markings are quite clearly developed. To our knowledge this is the first recorded instance where the pearlitic structure has been revealed by a plain vacuum etch. Whether this pearlitic relief has been developed by differential expansion in the layers of ferrite and cementite at the time of their formation or by a preferential volatilization and deposition of iron below the $A_{3,2,1}$ point, cannot easily be determined.

In Fig. 14, there is again evidence of the boundaries of a gamma structure that has been obliterated through the growth of the neighboring crystals. From Fig. 13, an idea can be obtained regarding the size to which one of these gamma crystals has grown during a vacuum treatment.

In order to prove that the outside layer of high-carbon steels, now of almost minute thickness, was composed of carbide-free ferrite, a portion that had received the above vacuum treatment, was etched in 4 per cent. nitric acid for 10 sec. Fig. 15 shows one alpha crystal that was covered sufficiently thick with ferrite to prevent the pearlitic structure from being etched; in the majority of the crystals, however, the pearlite is beginning to appear. The gamma boundaries have already begun to disappear. If etched slightly longer in the same reagent, a structure similar to that shown in Fig. 16 is obtained. The old gamma boundaries, in this instance, are quite clearly marked by the excess cementite that has collected in these boundaries at the high temperatures; the alpha crystals can easily be detected by the different orientation in the pearlite.

In connection with their work on high-carbon steels, the authors have noticed that specimens that have been heated several times in vacuo,

without attempting to remove the surface structure, gradually became coated with a lamellar gray crystalline deposit. Fig. 17 shows the extent to which this development has taken place on a 1.01 per cent. carbon steel. These masses lie on the surface of the austenitic crystals and apparently have been formed in the high-temperature range. Work is now in progress to ascertain the nature and cause of this substance.

Etching Below the A_3 Transformation

A piece of the same low-carbon steel that was previously heated to 1000° C. in vacuo was heated for 30 min. at 760° C., which conditions were recommended by Rawdon and Scott[7] for producing a maximum ferrite layer. It is their belief that at about this temperature the maximum amount of carbide is volatilized in proportion to the rate of diffusion of the carbide in the steel. They succeeded in obtaining, under these conditions, several layers of carbide-free ferrite crystals near the surface.

Somewhat different results were obtained by the authors, particularly as to the thickness of the ferrite layer. The surface relief, as shown in Fig. 18, was made up of alpha crystalline boundaries. On being etched, only ferrite crystals appeared, but they are very small in those areas formerly occupied by the pearlite. Deeper etching was impractical because of the pitting of the ferrite. The surface was copper plated and a cross-sectional structure obtained which showed that the pearlitic areas extended approximately to the surface, as is shown in Fig. 19. Sectional views were repeatedly made but the authors never obtained ferrite layers as deep as those obtained by Messrs. Rawdon and Scott. In fact, the same steel when held for 30 min. at 740° C. gave a ferrite surface similar to that shown in Fig. 18. But in this case the layer was so thin that the pearlite was uncovered when etched for 30 sec. in 4 per cent. nitric acid, as shown in Fig. 20. These experiments seem to strengthen the theory that the ferrite layer as well as the vacuum etching is produced by the volatilization and redeposition of iron.

Summary

The vacuum relief has been produced by the volatilization and redeposition of iron.

Three types of markings are visible when samples of steel are held at 1000° C. in vacuo for a few hours: A deeply marked polyhedral structure, which represents the final gamma boundaries; a fine clean-cut structure, which can be brought out more clearly by etching, that represents the alpha boundaries; an indefinite, and often partly obliterated, struc-

[7] *Loc. cit.*

ture that represents the boundaries of former gamma crystals that have been absorbed by crystalline growth.

The outside layer consists of ferrite as a result of the iron having been volatilized and redeposited below the temperature at which solid solution exists. Iron oxide will react with the carbides in steel at temperatures below 1000° C. to form carbon monoxide and pure iron.

Acknowledgments

The authors wish to thank all those at Watertown Arsenal who have assisted in the preparation of this paper, especially Dr. F. C. Langenberg through whose interest and advice this work was made possible.

DISCUSSION

J. W. Richards,* South Bethlehem, Pa.—If you take the temperature at 1,000° C., it shows that the percentage of CO which would be formed would be 92 per cent. of the mixture; according to Mr. Matsubara's data the pressure would be one and seven tenths atmosphere, and the coefficient of chemical equilibrium would be 30,000. So it is a very active reaction and explains quantitatively the mechanics of the reaction and the rate at which it proceeds at different temperatures.

On page 396 is a statement which I am inclined to question. It is: "To further develop this theory, it would be expected that iron or steel, held for any extended length of time at a temperature above the gamma range, would show a well-marked development of the gamma crystals.

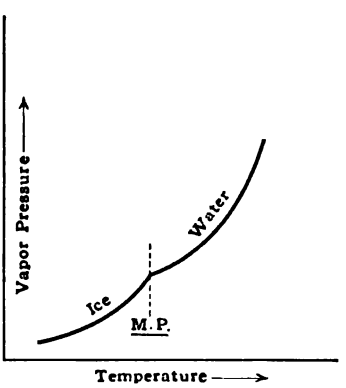


Fig. 21.

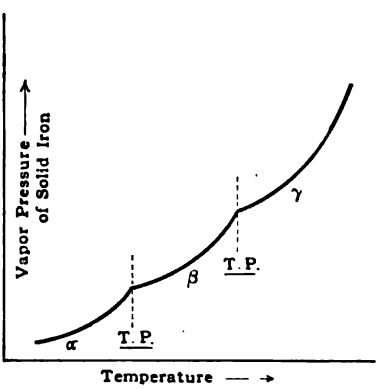


Fig. 22.

Not only will the vapor pressure be greatly raised, due to the higher temperatures, but one may logically believe that the vapor pressure of

* Professor of Metallurgy, Lehigh University.

gamma iron will be much greater than that of the lower allotropic forms."

Then the author proceeds to develop the idea that the pressure of the gamma iron is greater. It seems to me, from what study I have made, it ought to be less. Fig. 21 shows that when ice passes into water there is a cusp in the vapor tension curve. If ice could exist above the melting point *M.P.*, its vapor tension would be higher than that of water at the same temperature; inversely, at temperatures below *M. P.*, water has a higher vapor tension than ice. Fig. 22 shows the analogous transitions of alpha into beta and gamma iron. The transformation temperatures *T. P.* are analogous to a melting point, in that energy is there absorbed and the vapor tension curves must change in the directions shown. Therefore, at temperatures above the lower *T. P.* alpha iron has a higher vapor tension than beta iron, and at temperatures above the higher *T. P.* beta iron will have a higher vapor tension than gamma iron. These conclusions must be thermodynamically the correct ones.

The energy absorbed at each of these points being about 5 calories per gram of iron, or 280 calories per gram atom weight, I have calculated the vapor tensions of the three different varieties of iron in the solid state as being:

$$\text{Pure iron, } \gamma \text{ variety: } \log p_{mm} = -\frac{15{,}840}{T} + 8.84$$

$$\text{Pure iron, } \beta \text{ variety: } \log p_{mm} = -\frac{15{,}913}{T} + 8.90$$

$$\text{Pure iron, } \alpha \text{ variety: } \log p_{mm} = -\frac{15{,}974}{T} + 8.96$$

I do not know whether these formulas are going to be of any use to anybody, but they would express quantitatively the difference between the vapor pressures of alpha, beta, and gamma iron, and they would at transformation points show the same pressure. Therefore it would seem to me that the vapor pressure of the gamma iron at temperatures of 1000°, which is higher than the higher transformation point, ought to be less than that of the other iron. I do not know whether the author can revise his explanations in view of that or not.

G. K. Burgess,* Washington, D. C.—I have no brief for this paper but the author states specifically that the facts are as he would indicate for the allotropic forms of the phosphorus.

I am not certain as to the shape of the curve in the beta region. If that curve is tipped the other way a little bit, why then, of course, the vapor pressure of the lower region may be lower in the gamma region than the gamma itself. We ordinarily would assume the curves to be

* Chief, Division of Metallurgy, Bureau of Standards.

as have been indicated but I am not certain what the vapor-pressure curve for the iron is in the region immediately below the gamma region. Such a thing is possible. If it exists already for two allotropic forms, which I am not certain of, the author's statement being correct, it is also possible that it may also be correct for iron.

J. W. RICHARDS.—Incidentally, I figured out in connection with the vaporization of the iron that at 1000° C. the vapor pressure of iron is 0.00025 mm. The deposit was said to contain some copper. The vapor pressure of copper at the same temperature would be 0.00063. The vapor pressure of manganese would be, at the same temperature, 0.00800, very much higher. So if there were equal quantities present, you would probably have more manganese vaporized than copper and more copper vaporized than iron. I think these figures express the relative volatility of those three elements at 1000° and they are volatile at that temperature since there was found both manganese and copper in the deposit of iron.

G. K. BURGESS.—There is one point I would like to make for the author's paper. On page 393, he says; "No traces of either carbon or sulfur in the free or combined state were found and it is believed that the loss in these elements could be accounted for in the gaseous oxide products evolved, such as carbon monoxide and sulfur dioxide." He said that they were collected in the form of their soluble salts. I would like to know how he has tried to collect his carbon. He has not sufficiently explained that.

R. O. GRIFFIS,* Middletown, Ohio (written discussion).—Ordinarily the three distinct structures so well shown in Figs. 6, 7, and 14, are not in the same plane, which makes it difficult to find an area where it is possible to show the three structures at once micrographically. Some years ago I conducted a series of tests to determine the effect of hydrogen annealing upon the sonims found in bar crops from the top portions of low-carbon ingots made by the basic open-hearth process. In the first test, ordinary commercial hydrogen was passed over the polished samples heated to a temperature of 950° C. in a tubular electric furnace. As no precaution was taken to purify the hydrogen, after the run it was found that the hydrogen was so badly contaminated with moisture that instead of the oxide inclusions being reduced, the polished surfaces of the specimens were oxidized.

Fig. 23 shows the microstructure of one of the specimens as it came from the furnace. Heavy black boundaries of the gamma iron crystals are clearly shown and the characteristic twinning of gamma iron is evident. Fig. 24 shows the same spot after the oxide film was partly

* Assistant Research Metallurgist, American Rolling Mill Co.

removed by polishing. Fig. 25 is the same spot after further polishing and etching lightly with 3 per cent. nitric acid in ethyl alcohol. Fig. 26 shows the same area after repolishing and etching. This micrograph

FIG. 23. ×100.

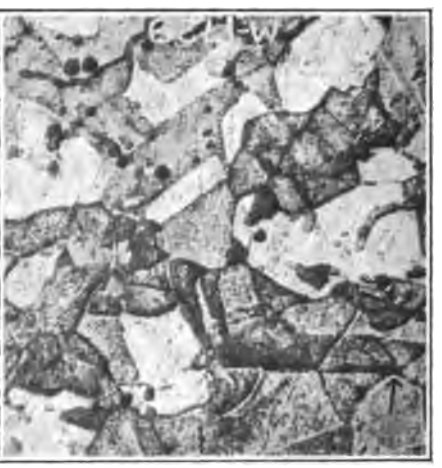


FIG. 24. ×100.

FIG. 25. ×100.

FIG. 26. ×100.

shows two networks of grain structure, the normal dark boundaries, representing the final alpha iron structure, and the faint white markings coinciding with heavy dark gamma boundaries shown in Fig. 23. By comparing Figs. 23 and 26, it will be seen that it would have been difficult without the aid of Figs. 24 and 25 to have identified the area as

being the same. A gamma grain in the lower right-hand corner has been marked by an arrow in each case.

From the manner in which this structure was produced, it seems that a redeposition of volatilized iron does not play an important role in the production of a heat relief, as the authors believe, for a constant stream of hydrogen passing through the apparatus would have carried off the volatilized iron. On the contrary, the evidence is in favor of the theories of a greater rate of volatilization at the grain boundaries and of a slight buckling of the surface due to the change in volume at the Ac_3 and Ar_3 transitions.

On page 406, the authors, referring to the third set of boundaries, which are very wide and more or less indistinct, state that they "have decided that they originated in the gamma range and actually represent gamma boundaries that formerly existed, but have been enveloped in the later crystalline growth." It is more probable that these are the alpha boundaries that existed just before the Ac_3 transformation. If the gamma grains grow as the temperature increases (and they probably do(why should any particular stage in the progress of this growth stand out more prominently than other stages and thus be shown by the wide, rather indistinct boundaries? If the boundaries are those of the pre-existing alpha grains, it is evident that the allotropic transformation is the primary cause of the heat relief. Fig. 18, shows that the alpha network brought out by heating in vacuo at 760° C., which is probably due to differential volatilization, is in no way similar to the two networks observed after the Ac_3 and Ar_3 transformations have taken place.

Microstructure of Iron and Mild Steel at High Temperatures

By Henry S. Rawdon * and Howard Scott, † Washington, D. C.
(New York Meeting, February, 1920)

The method of demonstrating the structure existing in a metal or alloy at high temperatures, by etching a polished sample after it has been heated to the desired temperature, is quite familiar to metallographists. The usual procedure[1, 2] is to heat the specimen, previously polished for microscopic examination, to the desired temperature, in a neutral atmosphere (hydrogen or nitrogen), then admit the etching gas (chlorine, hydrochloric acid or similar gas) for a few seconds, and finally, after flushing out the etching gas with the neutral one, cool the specimen in the neutral atmosphere. The pattern produced by etching at a definite temperature is usually taken as a record of the microstructure prevailing at that temperature. It has frequently been pointed out that changes in composition of the surface metal occur during the preliminary heating in the neutral atmosphere, so that the appearance produced by the etching at high temperature may not exactly represent the condition of the interior of the specimen. To overcome this uncertainty, the heating has sometimes been done in vacuo,[3] the etching gas being admitted when the desired temperature was reached, then pumped out and the specimen cooled in vacuo.

The studies of Rosenhain, Humfrey, and other workers [4,5,6,7,8] dem-

* Physicist, U. S. Bureau of Standards.

† Assistant Physicist, U. S. Bureau of Standards.

[1] N. Gutowsky: Uber die Structur des Stahlen bei hohen Temperaturen: *Metallurgie* (1909) **6**, 743.

[2] H. Hanemann: Über das Ätzen in Hoher Temperatur. *Inter. Zeit. Metallographie* (1912–13) **3**, 176.

[3] N. Tschischewsky and N. Schulgin: *Jnl.* Iron and Steel Inst. (1917) **95**, 189.

[4] W. Rosenhain and J. C. W. Humfrey: The Crystalline Structure of Iron at High Temperature. *Collected Researches*, Natl. Phys. Lab., Teddington (1910) **6**, 189.

[5] W. Rosenhain and J. C. W. Humfrey: The Tenacity, Deformation and Fracture of Soft Steel at High Temperatures. *Jnl.* Iron and Steel Inst. (1913) **87**, 219–315.

[6] J. C. W. Humfrey: The Intercrystalline Fracture of Iron and Steel. *Collected Researches*, Natl. Phys. Lab., Teddington (1913) **10**, 113. Also Iron and Steel Inst., *Carnegie Sch. Mem.* (1912) **4**, 80.

[7] W. Rosenhain and D. Ewen: Intercrystalline Cohesion in Metals, *Collected Researches*, Natl. Phys. Lab., Teddington (1913) **10**, 91. Also *Jnl.* Inst. Metals (1912) **8**, 149.

[8] Adolphe Kroll: The Crystallography of the Iron-carbon System. *Jnl.* Iron and Steel Inst. (1910) **81**, 304.

onstrate that surface changes in the steel occur even when the specimens are heated in vacuo. Such changes in themselves are sufficiently pronounced to record, in the appearance of the surface, the microstructure prevailing at the temperature at which the change took place. The surface configuration or pattern thus produced, to which various names (heat-relief, heat-etching, and vacuum etching) have been applied, has been explained by Rosenhain as being due to volatilization of the surface metal. This is more marked along the crystal boundaries than over the face of the crystal itself. The change in composition of the layer immediately adjacent to the surface of a steel sample when heated in vacuo or in a neutral atmosphere has also usually been attributed to volatilization. Howe[9] has offered an entirely new and striking explanation for this phenomenon, namely, that the change in composition of the surface layer is only local and the average composition of the specimen does not change. Upon cooling a sample of steel from a high temperature, the free constituent (ferrite or cementite as the case may be) is expelled to the outside of the mother austenite crystal and thus to the surface of the specimen in those crystals which form the exterior. By repeated heatings, the layer of expelled ferrite (in the case of low-carbon steels) is augmented until the specimen has the appearance of being decarburized at the surface.

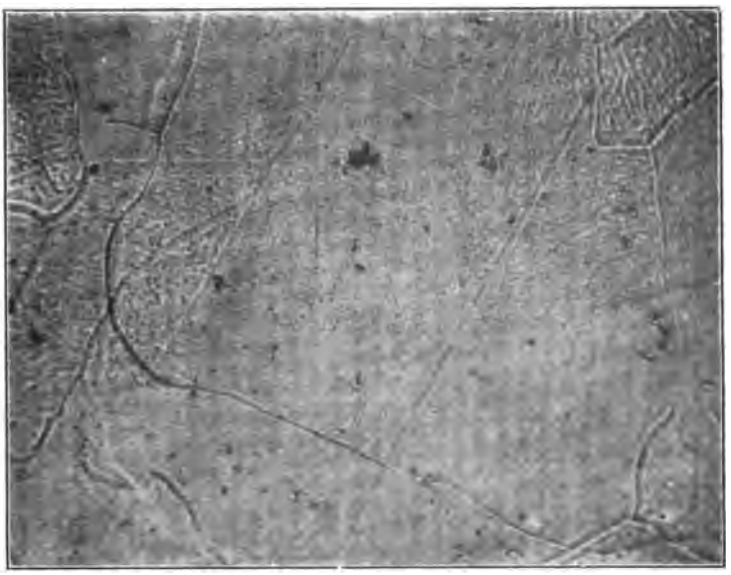
The examinations here described were made for the purpose of showing to what extent the change in composition of the surface layer, which usually accompanies heating in vacuo, affects the results of tests which may be made to reveal the microstructure existing at high temperatures. The results also throw some additional light upon the nature of the change in composition of the surface layer and also upon the formation of the surface pattern under heat-relief etching.

Method of Revealing Structural Changes Occurring at High Temperatures

Pure iron and low-carbon steel were chosen as typical materials for demonstration, since both materials show pronounced changes in structure accompanying some of the transformations which occur upon heating. The normal structure of each is familiar, and the microstructure at high temperature has been demonstrated by means of the etching method.

Pure Iron.—A remelted electrolytic iron having the following composition was used: carbon, 0.03 per cent.; sulfur, 0.002 per cent.; silicon, 0.009 per cent. By thermal analysis, the material was shown to have

[9] H. M. Howe: The Position of Ae_3 in Carbon-iron Alloys, Discussion. *Trans.* (1913) **47**, 659.



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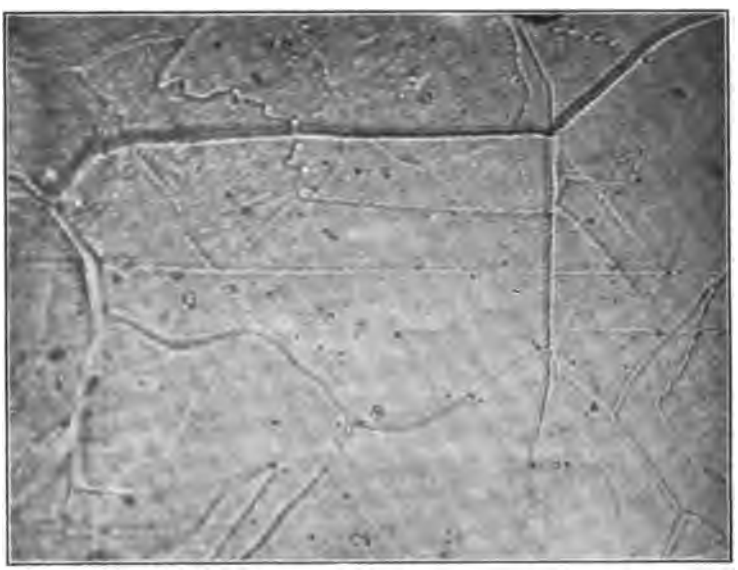
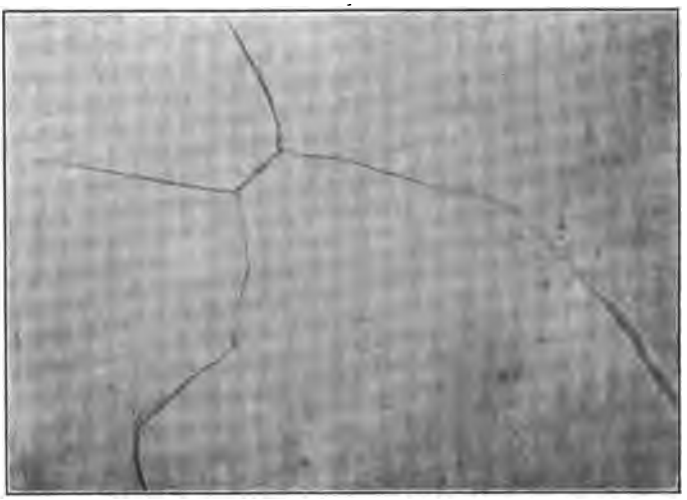


b

FIG. 1.—MICROSTRUCTURE OF PURE IRON ABOVE THE Ac_3 TRANSFORMATION.

BOTH MICROGRAPHS SHOW THE SURFACE APPEARANCE OF THE SAME MATERIAL, A SPECIMEN OF WHICH WAS HEATED FOR 30 MIN. AT 950° C. TWO NETWORKS INDICATING TWO DIFFERENT CRYSTALLINE ARRANGEMENTS ARE TO BE SEEN. THE ONE SHOWING THE TWINNED CRYSTALS IS THE STRUCTURE PREVAILING ABOVE A_3, THE OTHER, SUPERIMPOSED UPON THE FIRST, CORRESPONDS TO THE STRUCTURE AT LOWER TEMPERATURES. HEAT-ETCHED. ×500.

the following thermal characteristics: Ac_2, 768°; Ac_3, 910°; Ar_3, 900°; Ar_2 768° C. The specimens, which were of the size used for thermal



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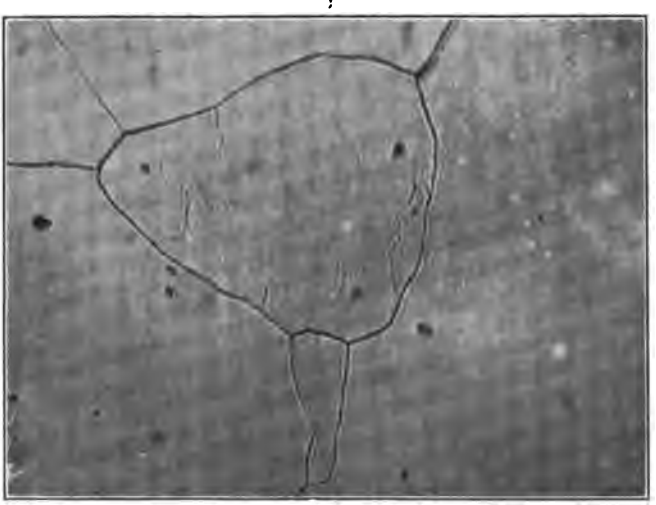

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FIG. 2.—MICROSTRUCTURE OF PURE IRON BETWEEN THE A_2 AND A_3 TRANSFORMATIONS

THE POLISHED SPECIMEN, REPRESENTED BY THE TWO MICROGRAPHS, WAS HEATED 30 MIN. AT 880° C., OR JUST BELOW A_3. THE APPEARANCE OF THE PREVIOUSLY POLISHED SURFACE REVEALS THE STRUCTURE, WHICH IS OF THE SAME TYPE AS THAT PREVAILING AT ORDINARY TEMPERATURES. THE EXCESSIVE VOLATILIZATION AT THE MARGINS OF THE GRAINS HAS CLEARLY DEVELOPED THE BOUNDARIES. HEAT-ETCHED. ×500.

analysis (approximately 3 gm.), were mounted on the end of a platinum platinum-rhodium thermocouple and heated in the evacuated tube of a

differentially heated furnace of the Rosenhain type[10] to the following temperatures: 950° C., above A_3, 880° C., between A_2 and A_3; 700° C., below Ac_1 (of steels). In each case the specimen was held for approximately 30 min. at the maximum temperature and then cooled in the evacuated furnace at an approximate rate of 0.15° per sec. by moving the specimen to the cold end of the tube. The surface of the specimens, after heating, showed no evidence of oxidation. In most cases, particularly those heated to the highest temperatures, the surface had a slightly roughened or matt appearance.

Fig. 1 shows the surface pattern produced by heating the iron above the Ac_3 transformation. Two distinct patterns are to be seen superimposed one upon the other. One of the patterns is similar in appearance to that of pure iron as ordinarily etched at room temperature; the other network contains numerous straight lines and many of the enclosed "grains" have the appearance of twinned crystals. This is clearly shown in Fig. 1*a*. The two long narrow crystals are the twinned layers of a much larger crystal, the boundaries of which can be faintly seen. Another network, outlining a second system of grains, is superimposed upon the twinned crystals. Fig. 1*b* shows similar features.

The network delineating the straight-sided polyhedral twinned crystals is a record of the structure of the γ iron, *i.e.*, the form existing above the A_3 transformation. The second network belongs to the crystal structure prevailing below this transformation, as seen in specimens heated to a temperature below A_3. Only one network is developed under such treatment, and this is identical with the second pattern of specimens heated above A_3. The specimen shown in Fig. 2 illustrates this, and also shows that no characteristic crystal form corresponds to the so-called β range. The appearance is the same as that of specimens heated to a temperature well below A_2 (Fig. 3) and also of samples polished and etched under ordinary conditions. This observation confirms that of Rosenhain and Humfrey, in this respect.

Fig. 3 shows the surface of a polished specimen heated to 700° C. The network outlining the arrangement of the crystals appears faintly even at this relatively low temperature.

The surface of freshly heated specimens often has a "matt-finish" appearance and, when viewed at an oblique angle, is seen to be considerably roughened. The volatilization occurring at high temperatures, as shown in Fig. 1*a*, accounts partly for the matt-finish. It will be noted that the volatilization develops rather well-defined "etching pits" on the surface, by means of which the structural orientation within the twin crystals relative to the mother crystal is plainly shown. The

[10] H. Scott and J. R. Freeman, Jr.: Use of Modified Rosenhain Furnace for Thermal Analysis. *Bull.* 152 (Aug., 1919). Also "Pyrometry," 214, A. I. M. E., 1920.

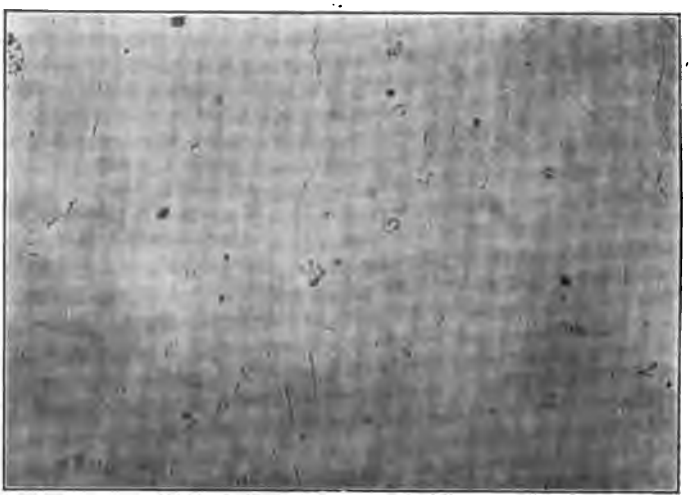


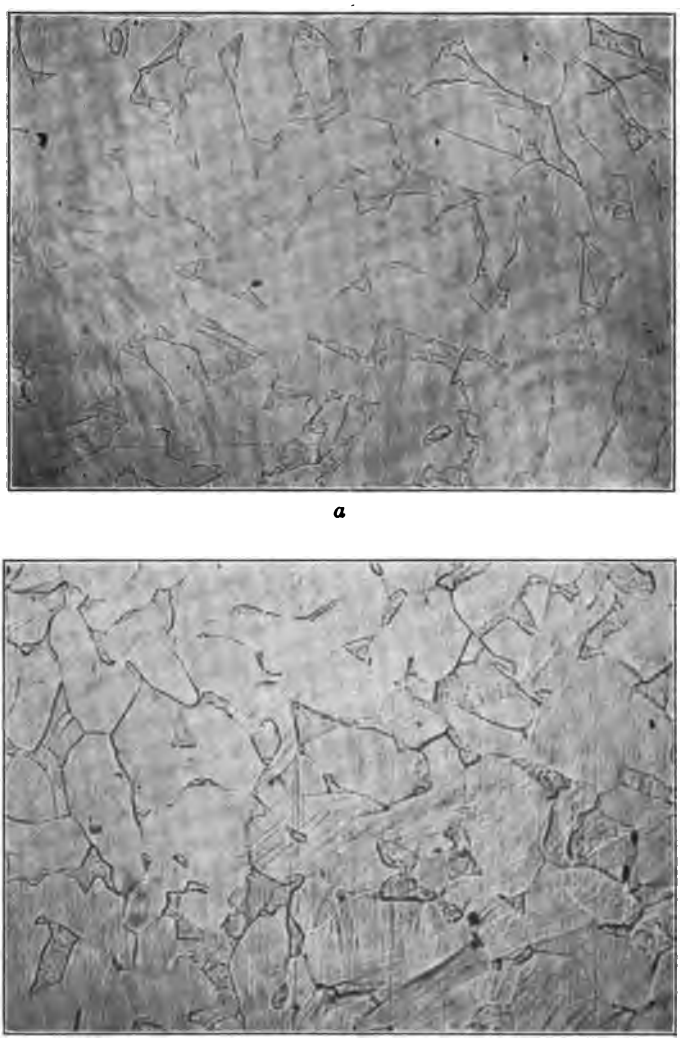
FIG. 3.—MICROSTRUCTURE OF PURE IRON JUST BELOW THE TRANSFORMATION TEMPERATURES.

A POLISHED SPECIMEN OF THE MATERIAL WAS HEATED FOR 30 MIN. AT 700° C. THE VOLATILIZATION AT THE GRAIN BOUNDARIES, THOUGH SLIGHT, HAS BEEN SUFFICIENT TO REVEAL THE STRUCTURE, WHICH IS OF THE SAME TYPE AS THAT EXISTING BETWEEN A_2 AND A_3. HEAT-ETCHED. ×500.

FIG. 4.—MICROSTRUCTURE OF PURE IRON AT HIGH TEMPERATURES.

THE MICROGRAPH SHOWS A SECTION PERPENDICULAR TO THE POLISHED AND HEAT-ETCHED SURFACE OF FIG. 1. A LAYER OF ELECTROLYTIC COPPER WAS DEPOSITED TO PRESERVE THE EDGE DURING THE POLISHING OF THE SPECIMENS. THE ORIGINALLY RECTILINEAR EDGE HAS BEEN CHANGED INTO A SERIES OF UNDULATIONS BY THE VOLUME CHANGES AT THE TRANSFORMATION TEMPERATURE. ETCHING, 2 PER CENT. ALCOHOLIC NITRIC ACID. ×500.

roughened appearance is largely due to a "buckling" of the surface of the individual crystals. Fig. 4, a section perpendicular to the polished



a

b

FIG. 5.—MICROSTRUCTURE OF LOW-CARBON STEEL JUST BELOW THE Ac_1 TRANSFORMATION.

a. THE POLISHED SPECIMEN WAS HEAT-ETCHED BY HEATING IT FOR 30 MIN. AT 700° C. *b*. THE POLISHED SPECIMEN WAS DISTORTED SUFFICIENTLY TO SHOW SLIP BANDS AND THEN HEAT-ETCHED AS IN (*a*). THE SLIP BANDS STILL PERSIST. HEAT-ETCHING IN BOTH CASES. ×100.

surface which was exposed to the heat, demonstrates the distortion that occurs; the boundary, *i.e.*, the trace of the polished flat surface, originally rectilinear, now consists of a series of undulations. Specimens heated

to a temperature a little below A_3 show an irregular branching network within the grains themselves (Fig. 2*b*). This is often seen in pure iron

a

b

FIG. 6.—MICROSTRUCTURE OF LOW-CARBON STEEL JUST BELOW THE Ac_1 TRANSFORMATION.

a. THE MATERIAL OF FIG 5*a* WAS SLIGHTLY POLISHED TO REMOVE THE EFFECTS OF HEAT-ETCHING, AND THEN ETCHED WITH 2 PER CENT. ALCOHOLIC NITRIC ACID. THE MATERIAL SHOWS THE NORMAL STRUCTURE FOR THIS CLASS OF STEEL. ×100.

b. A SPECIMEN SIMILAR TO FIG. 5*a* WAS ETCHED WITH 2 PER CENT. ALCOHOLIC NITRIC ACID DIRECTLY AFTER BEING HEAT-ETCHED. THE SURFACE ETCHES AND DARKENS IMMEDIATELY. ×100.

after ordinary etching for microscopic examination, particularly if the sample has been strongly heated previously, for example, specimens

which have been heated several times for thermal analysis curves. Whether this bears any relation to the β change has not yet been determined.

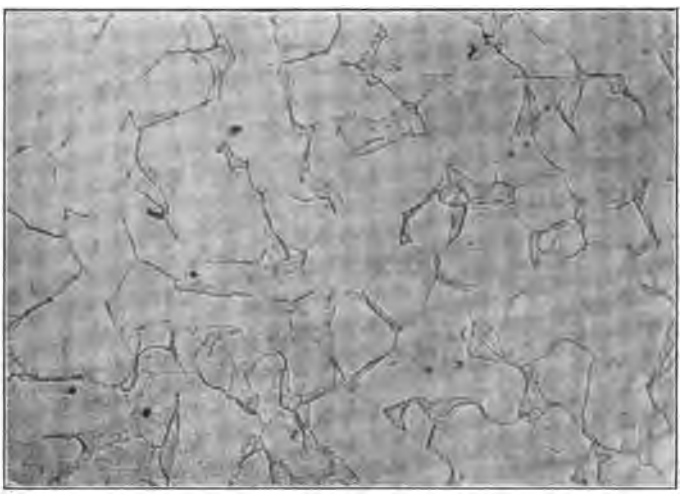
Low-carbon Steel.—A synthetic low-carbon steel[11] having the following composition was selected as representative of this class of material: carbon, 0.18 per cent.; silicon, 0.007 per cent. It had the following thermal characteristics: Ac_1, 738°; Ac_2, 769°; Ac_3, 840°; Ar_3, 792°; Ar_2, 769°; Ar_1, 700° C. The specimens, first polished for microscopic examination, were heated in vacuo in the same manner as the pure iron, to the following temperatures, and were held approximately 30 min. at the maximum temperature: 950° C. above Ac_3; 760° C., above Ac_1; 700° C., below Ac_1.

Fig. 5*a* shows the appearance of a specimen heated to 700° C., just below the transformation Ac_1. Even at this temperature the heat-relief has been sufficient to indicate clearly the islands of pearlite. Fig. 5*b* is a specimen which, after polishing, was distorted enough to develop slip bands and then heated to 700° C. The slight roughening of the surface, due to the slipping, still persists at this temperature and shows that no marked volatilization has occurred at the surface.

Fig. 6*a* shows the specimen of Fig. 5*a* after it had been polished slightly to remove the effects of the heat-relief and then etched; it has the usual appearance of low-carbon steel. When the specimen is etched directly after heating, without any supplementary polishing, the surface darkens almost immediately and gives the appearance shown in Fig. 6*b*. A similar pronounced darkening of ferrite, upon etching, is often observed when a specimen is finished on a polishing wheel which has been allowed to become dry, so that the surface heats considerably. Upon heating a polished specimen of this material above the Ac_1 transformation, the surface takes on the appearance shown in Fig. 7*a*, which is very similar to that produced by heating below Ac_1; the position of the pre-existing pearlite islands is clearly indicated. It will be noted that the network which marks the boundaries of the ferrite crystals is now continuous through the pearlite areas instead of around them; this is best seen at a higher magnification, as in Fig. 7*b*. When the surface is etched, without any polishing, the appearance is the same as is shown in Fig. 6*b*. However, when the surface is slightly polished and then etched, no darkening results nor is there left any trace of the pattern developed by heat-relief. The material constituting the surface is pure ferrite (Fig. 8*a*); all the pearlite has been removed to a considerable depth, as is shown in Fig. 8*b*, a section of the specimen perpendicular to the polished face, the normal appearance of the material being seen in the lower portion of the micrograph. The boundary between the outer, or carbonless, metal and the inner normal material is clearly defined, showing that the change from the outer zone to the unchanged metal of the interior is very abrupt.

[11] An alloy of iron and carbon prepared according to the method given by U. S. Bureau of Standards. *Sci. Paper* 266.

Fig. 9*a* illustrates the pattern developed by heat-relief on the polished surface by heating above the Ac_3 transformation. The more clearly defined network, corresponding to the γ condition, is superimposed



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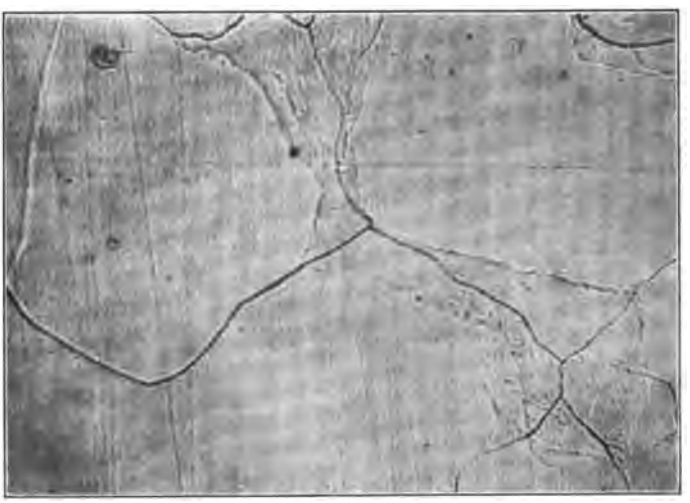

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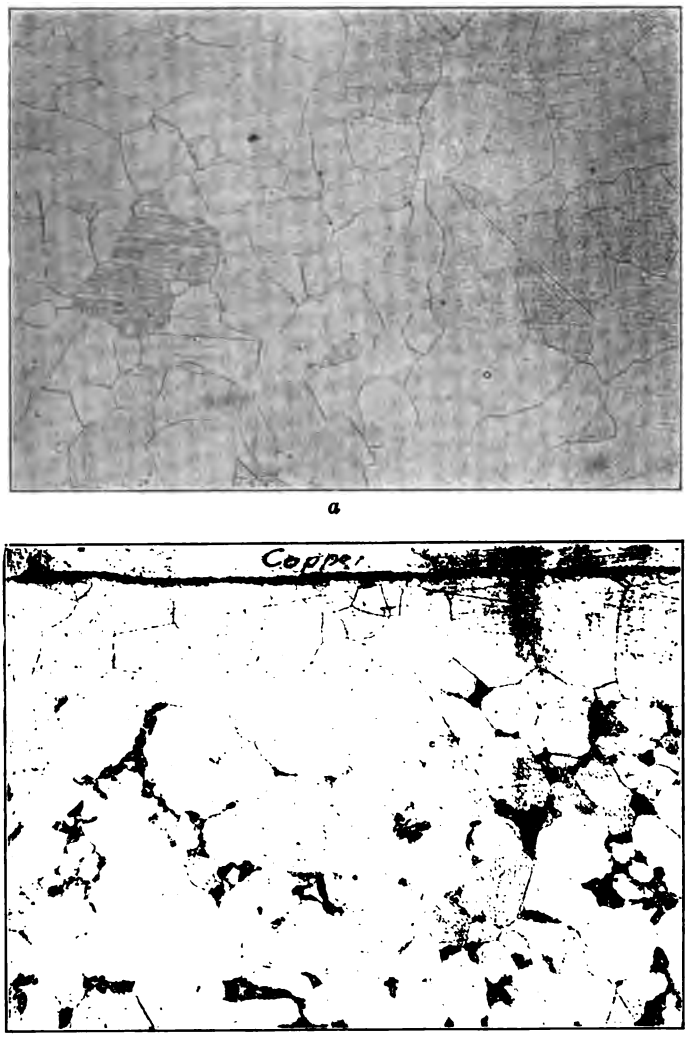
FIG. 7.—MICROSTRUCTURE OF LOW-CARBON STEEL JUST ABOVE THE Ac_1 TRANSFORMATION. THE POLISHED SPECIMEN WAS HEAT-ETCHED BY HEATING 30 MIN. AT 760° C.
a. BOTH FERRITE AND PEARLITE ARE CLEARLY SHOWN. ×100.
b. THE BOUNDARIES OF THE FERRITE GRAINS EXTEND THROUGH THE PEARLITE ISLANDS. ×500.

upon a less distinct one which shows the characteristic outlines of the α crystals; this is more plainly seen in Fig. 9*b*. The polished specimen in this instance was etched to reveal its initial structure and then heated for

30 min. at 1000° C., or well above the temperature of the Ac_3 change. The roughening of the surface, corresponding to the islands of pearlite



a

b

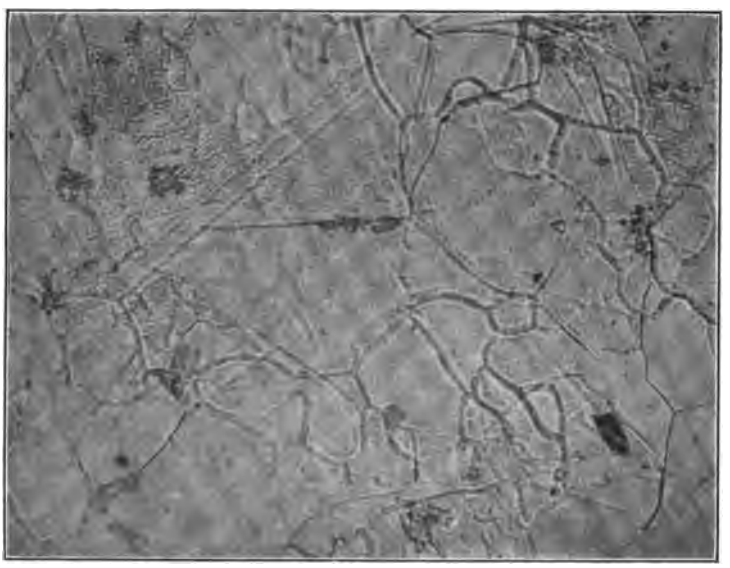
FIG. 8.—MICROSTRUCTURE OF LOW-CARBON STEEL JUST ABOVE THE Ac_1 TRANSFORMATION.

a. THE SPECIMEN OF FIG. 7*a* WAS SLIGHTLY POLISHED AND ETCHED WITH 2 PER CENT. ALCOHOLIC NITRIC ACID. THE SURFACE METAL IS PURE FERRITE. ×100.

b. SECTION OF THE SPECIMEN SHOWN IN *a* TAKEN PERPENDICULAR TO THE HEAT-ETCHED SURFACE. ETCHING, 2 PER CENT. ALCOHOLIC NITRIC ACID. A LAYER OF ELECTROLYTIC COPPER WAS DEPOSITED TO PROTECT THE EDGE DURING POLISHING. THE PEARLITE HAS BEEN REMOVED FROM THE SURFACE METAL, BY THE HEATING, FOR A CONSIDERABLE DEPTH. ×100.

shown by the initial etching, still persists. Upon this pattern two others are superimposed, showing respectively the crystalline condition above

a

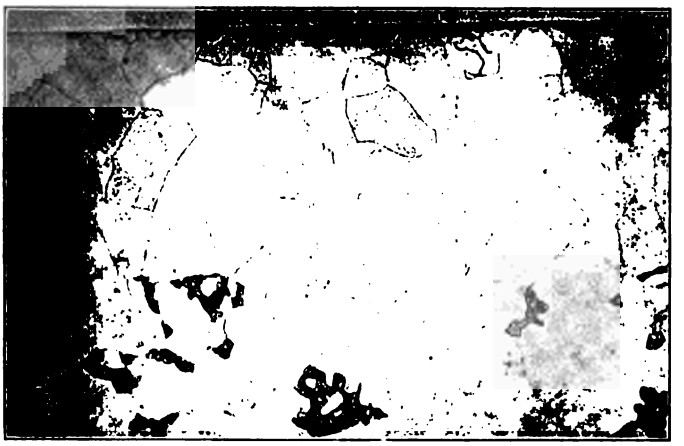


b

FIG. 9.—MICROSTRUCTURE OF LOW-CARBON STEEL ABOVE THE Ac_3 TRANSFORMATION.

a. THE POLISHED SPECIMEN WAS HEAT-ETCHED BY HEATING 30 MIN. AT 950° C. TWO PATTERNS CORRESPONDING TO THE α AND THE γ FORMS (COMPARE FIG. 1) ARE TO BE SEEN. ×500.

b. THE POLISHED SPECIMEN WAS ETCHED WITH 2 PER CENT. NITRIC ACID BEFORE HEATING AT 1000° FOR 30 MIN. THE ORIGINAL PEARLITE PATTERN SHOWN BY THE FIRST ETCHING HAS PERSISTED THROUGHOUT THE HEATING; UPON THIS TWO OTHER PATTERNS SIMILAR TO THOSE IN *a*, HAVE BEEN SUPERIMPOSED. ×500.



a

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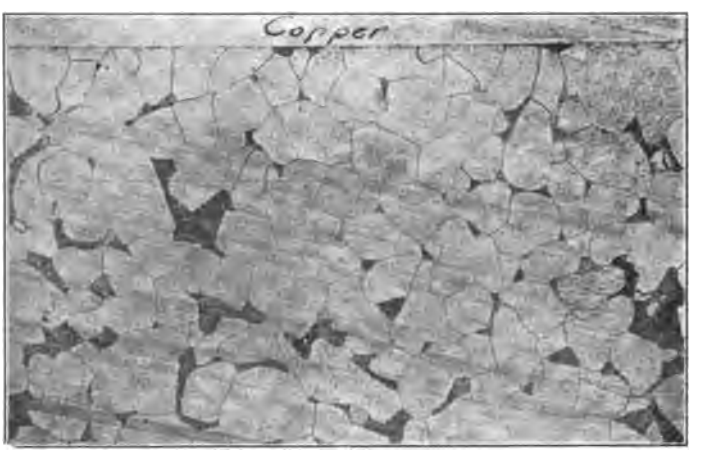


c

FIG. 10.—SURFACE CHANGES PRODUCED BY HEATING IN VACUO. ETCHING, 2 PER CENT. ALCOHOLIC NITRIC ACID.

a. HEATED FOR 30 MIN. ABOVE THE Ac_1 TRANSFORMATION (760° C.).
b. HEATED JUST BELOW THE Ac_2 TRANSFORMATION (820° C.).
c. HEATED ABOVE THE Ac_3 TRANSFORMATION (890° C.).

Ac_3 on heating, and below Ac_3 on cooling. The twin crystal (Fig. 9*b*), which had its origin when the steel was in the γ state, is seen to cut through the pre-existing islands of pearlite and to bear no relation to them. It should be borne in mind, however, that the carbide has been removed from the surface material, probably before the change to the γ state was brought about, as has been described above.

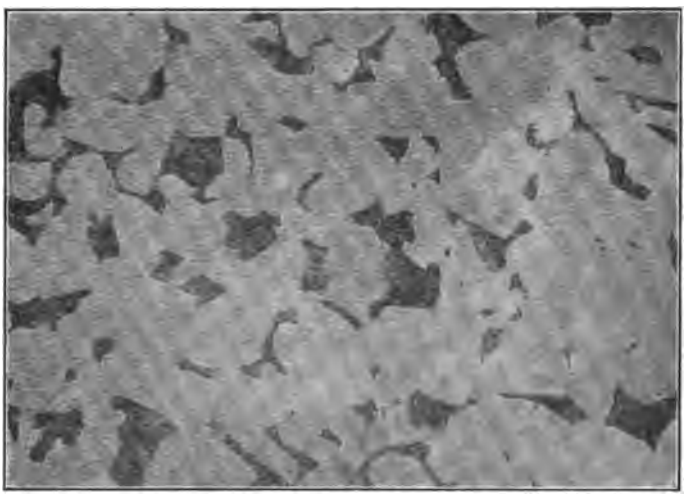
Nature and Extent of the Surface Changes upon Heating

The magnitude of the change (apparently decarburization) which occurs in some samples (Fig. 8) makes the explanation offered by Howe[12] appear inadequate. In order to show clearly the nature of the change, and to test his explanation, a series of specimens of the low-carbon steel previously used were heated for 30 min. in vacuo at the following temperatures: 760° C. above Ac_1; 820° C. just below Ac_3; 890° C. above Ac_3. The specimens were cooled in the furnace at the same rate as the previous ones. In each case the carbonless layer varies considerably in thickness on the same specimen; the maximum thickness of this changed layer, in specimens heated at the three temperatures stated above, is shown in Fig. 10. In the specimen heated at the lowest temperature, the decarburized layer is more pronounced than in those heated for the same period at higher temperatures. This is not to be attributed to a greater loss of carbon at the lower temperature, but rather to an increased rate of diffusion of carbide in iron at higher temperatures, by which any change at the surface, due to loss of carbon, is masked by a replenishment from the interior.

Fig. 11 shows the condition at the surface and near the center of a specimen (low-carbon steel previously used) heated continuously for 4 hr. above Ac_3, 990° C. being the maximum temperature. The structure of a sample of the same material, previously used for a series of four thermal curves, which had been held above the Ac_3 temperature for a total of 4 hr., is shown in Fig. 12. The thickness of the altered surface layer of the sample heated intermittently is somewhat greater than that of the specimen heated continuously for 4 hr. above the Ac_3 transformation temperature. The carbon content of the interior, however, as estimated from the structure, is slightly less in the specimen heated continuously than in the other one. This apparently contradictory behavior of the more strongly heated specimen is to be interpreted as further evidence of the part played by diffusion in masking the change which occurs at the surface. By comparing Figs. 10*a* and 11*a*, it will be noted that a much more marked change is produced in the surface metal by a short period at the lower temperature (30 min. at 760° C.) than by prolonged heating at a higher temperature (240 min. at 990° C.). Whether

[12] *Loc. cit.*

a

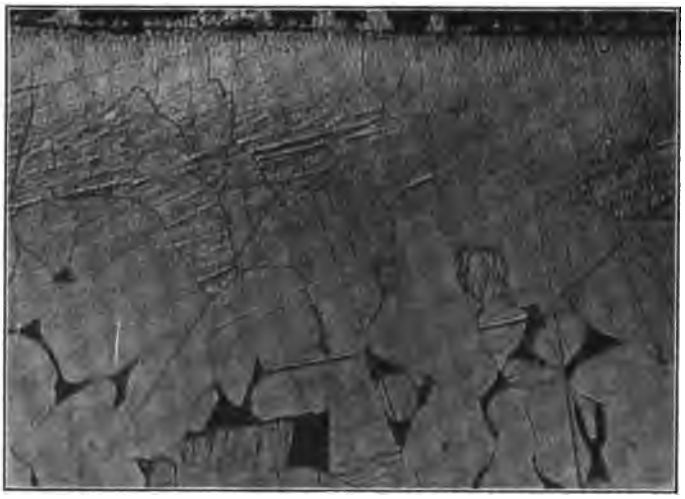


b

FIG. 11.—SURFACE CHANGES PRODUCED IN LOW-CARBON STEEL BY HEATING ABOVE THE A_3 TRANSFORMATION. A POLISHED SPECIMEN WAS HEATED CONTINUOUSLY FOR 4 HR. ABOVE THE Ac_3 TRANSFORMATION TEMPERATURE. THE HEAT-ETCHED SURFACE WAS THEN PROTECTED WITH A DEPOSIT OF ELECTROLYTIC COPPER AND THE SPECIMEN WAS CUT PERPENDICULAR TO THIS FACE. ETCHING 2 PER CENT. ALCOHOLIC NITRIC ACID. ×500. THE MICROGRAPH REPRESENTS:

a. EDGE OF THE SECTION, SHOWING THE THICKNESS OF THE CARBONLESS LAYER.

b. AVERAGE STRUCTURE AT THE CENTER OF THE SPECIMEN.



a

b

FIG. 12.—SURFACE CHANGES PRODUCED IN LOW-CARBON STEEL BY HEATING ABOVE THE Ac_3 TRANSFORMATION. THE SPECIMEN HAD BEEN USED FOR A SERIES OF THERMAL CURVES AND WAS HEATED FOUR TIMES TO 950° C., *i.e.*, ABOVE THE Ac_3 TRANSFORMATION TEMPERATURE; THE TOTAL PERIOD ABOVE THIS TEMPERATURE WAS 4 HR. THE SPECIMEN WAS TREATED AS FOR FIG. 13, WITH WHICH THIS FIGURE SHOULD BE COMPARED. ETCHING, 2 PER CENT. ALCOHOLIC NITRIC ACID. ×500.

a. CARBONLESS SURFACE LAYER.

b. AVERAGE STRUCTURE OF THE CENTRAL PORTION.

a

b

FIG. 13.—SURFACE CHANGES PRODUCED IN HIGH-CARBON STEEL BY HEATING IN VACUO ABOVE THE Ac_3 TRANSFORMATION.

THE SPECIMEN WAS PREPARED FOR EXAMINATION SIMILARLY TO THOSE OF FIGS. 11 AND 12. THE THERMAL TREATMENT WAS SIMILAR TO THAT OF THE SPECIMEN OF FIG. 12. ETCHING, 2 PER CENT. ALCOHOLIC NITRIC ACID. ×500.

a. THE AVERAGE SURFACE CONDITION IS SHOWN. THE CEMENTITE ENVELOPES DISAPPEAR AT SOME DISTANCE BELOW THE SURFACE; IN THE ORIGINAL CONDITION OF THE SPECIMEN THEY EXTENDED TO THE SURFACE. CEMENTITE HAS BEEN REMOVED FROM THE SURFACE.

b. IN A FEW EXCEPTIONAL SPOTS, A THIN WHITE (PROBABLY FERRITE) LAYER FORMED AT THE SURFACE. ETCHING WITH HOT SODIUM PICRATE SHOWED THAT THIS LAYER WAS NOT CEMENTITE.

this difference in the rate of diffusion is due entirely to temperature or partially to the allotropic condition of the iron, α or γ, can only be conjectured.

Fig. 13*a* shows the surface change induced in a high-carbon steel by heating four times in vacuo to a temperature above the Ac_3 transformation (950° C.). The steel had the following composition: carbon, 1.28 per cent.; manganese, 0.23, phosphorus, 0.017; sulfur, 0.017; silicon, 0.23 per cent. The cementite-grain envelopes do not extend entirely to the surface, as they did originally, but gradually diminish in thickness and disappear at some distance below the surface. In no case was an accumulation of cementite found, such as Howe's explanation would require. In a few areas a very thin layer of ferrite was found to have formed, as shown in Fig. 13*b*. The conclusion is evidently warranted that the change of structure of the surface metal heated in vacuo represents loss of carbon.

Interpretation of Results

It may properly be asked, to what extent are the etching indications of steel at high temperature vitiated by changes of composition that occur in the surface metal upon heating. The results previously described show that no decarburization below the temperature of the A_1 transformation can be detected. This is due to the physical form in which the carbon exists; not until the carbon (as carbide) is in the state of a solid solution in the iron, *i.e.*, above A_1, is there any appreciable change in the exposed surface metal. Below the A_1 transformation, the carbon occurs in the form of a definite crystalline compound and the loss upon heating may be entirely neglected.

A very marked change, however, occurs upon heating a specimen just above the A_1 transformation, when the carbon passes from the form of crystalline cementite to a solution (of cementite) in the iron. In this form it quite readily volatilizes from the surface, so that a pronounced carbonless layer is soon formed in specimens (low-carbon steel) that are held for periods no greater than 30 min. at this temperature. The method of heat-etching, however, serves to record the structure both before and after the change has taken place. The pronounced differential expansion of pearlite and ferrite at the A_1 transformation will partly account for this. The fact that at temperatures below A_1 the structure is clearly revealed by heat-etching, however, shows that this is not the sole cause, but that the slight general volatilization which occurs, together with the slight differences in the rate of thermal expansion of pearlitic steel and iron (ferrite) are sufficient to record clearly and definitely the structure of the metal. The volatilization of iron is sufficiently pronounced at the crystal boundaries to show them clearly, but across the face of the crystals there is very little loss, as is proved by the persistence of slip bands, upon

heating. That the ferrite is changed somewhat, is shown by its increased tendency toward oxidation. Upon slight etching with nitric acid, a distinct oxide film readily forms, coloring the ferrite very dark.

Specimens heated to temperatures higher than the A_1 transformation show a carbonless layer, which becomes thinner as the temperature is increased. This is properly to be attributed to the increased rate of diffusion of carbide in iron, by which the change at the surface is masked. The results obtained by etching specimens at the higher temperatures (heat-etching or otherwise) are more truly indicative, therefore, of the structure of the interior than those at lower temperatures, *e.g.*, just above A_1. That the loss of iron by volatilization across the face of the crystals is very slight, even at high temperatures, is proved by the persistence of the slight roughening due to preliminary etching throughout the entire period of heating. The loss by volatilization is of a magnitude sufficient to show the crystalline structure by the production of etching pits; at the crystal boundaries the loss is much greater. In addition, the carbide is removed to an appreciable depth on all the exposed faces of the specimen.

Summary

1. When polished metal specimens are heated in vacuo, a record of the structure existing at the particular temperature used is inscribed on the polished surface of the specimen. This record consists of a slight roughening due to volatilization and to a slight "buckling" of the surface, due to the volume change accompanying the transformation. The terms heat-relief, heat-etching, and vacuum-etching have been applied to this method of developing the microstructure.

2. By means of heat-relief the structure of iron and steel at high temperatures is readily revealed. This is a much simpler method than the high-temperature etching often used. It appears probable that much of the effect usually attributed to etching at high temperature is due to the heating itself.

3. An appreciable change of composition and structure of the surface metal occurs in steel, upon heating. This is strongly marked just above the A_1 transformation, and becomes less so upon heating to higher temperatures, due to the increased rate of diffusion of carbon (as carbide) in iron. The structure revealed on the surface by heat-relief, or by high-temperature etching, is less representative of the interior at temperatures just above the A_1 transformation than at any other temperatures.

4. The change in composition of the surface layer of steel heated to high temperatures in vacuo is to be explained as due to volatilization of the carbide. No appreciable change takes place until the carbide enters into solid solution in the iron, *i.e.*, above the A_1 transformation.

5. The volatilization of iron from the surface, upon heating, is very slight. Polished specimens of iron and steel, etched before being heated, retain the slight roughening due to the etching, even after pronounced heating. The volatilization of iron at the crystal boundaries is much more rapid than across the face of the crystal.

DISCUSSION

E. E. THUM,* New York, N. Y.—Since the authors have mentioned Doctor Howe's ideas regarding the expulsion of excess insoluble constituent to the boundaries of austenite grains, a brief consideration of this theory may be of interest. In his recent book, "The Metallography of Steel and Cast Iron," page 280, he cites the following facts to support his proposed mechanicalized transport of exotics, which might be described as an "elbowing" effect.

1. Those constituents appearing as needles in Widmanństättian bands are in that arrangement due to an expulsion to the octahedral cleavages of austenite rather than to an inherent crystallinity of the cementite or ferrite itself. The former is described as being orthorhombic, assuming the form of a rhombohedron, while Osmond and Cartaud find sublimed crystals of both α and β iron to be cubic.

2. Excess constituent will be found at the former location of slip bands after annealing strained metal.

3. Slag particles are at boundaries because crystals of austenite growing from a mother liquor push them away.

4. As slag is posited by "elbowing," its later frequent accompaniment of ferrite (or cementite) borders must have been caused by a like action.

5. Ferrite (or cementite) is extruded to the borders of austenite crystals upon cooling through the critical range, thus forming the well-known network shown in photomicrographs.

6. Excess constituent is by the same action extruded to all exposed surfaces, whether outer skin or inner cavities.

Presumably Doctor Howe would be willing to admit that there is another way to explain the migration of excess constituent, rather than by an elbowing effect; in fact, I think that all of his reasons, with the exception, possibly, of the last, might well be explained otherwise. In other words, excess constituent migrates to pre-formed nuclei of the same substance, much as a crystal grows in aqueous solution, and the movement of substances through solution (solid or liquid) is a matter of equilibrium; that is, continual dissolution at one place of low concentration and redeposition in another place at higher concentration rather than a mechanical transportation of the substance en masse.

* Associate Editor, *Chem. & Met. Eng.*

His statement that internal cavities are lined by ferrite in hypoeutectoid and cementite in hypereutectoid steels is rather a poser to any one who does not accept his idea of the elbowing effect. The experiments of the present paper, showing a pronounced decarburization when heating either grade of steel, leave one somewhat bewildered by the imposing evidence cited by Doctor Howe of cementite's migration to superficies during heating. On the other hand, the proponent of diffusion might ask him to cite some instance where austenite has been able to transport, bodily, a slag inclusion, or some insoluble constituent. Certainly the grain boundaries in Figs. 1a, 2b, 6a, and 7b appear to be entirely independent of the black spots, presuming them to represent non-metallic inclusions. If austenite will elbow out cementite or ferrite, as the case may be, it certainly ought to elbow out a particle of sulfide or any other foreign matter that might be there. On the other hand, diffusion is powerless to move an insoluble substance. So that the real test of the problem would be to discover some place where an insoluble constituent has been moved.

I am not familiar with any instance of that sort; in fact, I have been told by Doctor Giolitti that he has investigated the matter carefully and has proved to his own satisfaction that slag is not moved after heat treatment. Doctor Stead, I believe, says, when describing some of his experiments on the diffusion of phosphorus, that after long-time annealing he was able to break up all dendritic structure and to equalize phosphorus throughout the metal, but he states explicitly that even then non-metallic inclusions were not changed in location.

W. F. GRAHAM, Plainfield, N. J.—Do the small ferrite particles shown in the hardened tool steel occur only if the steel is hardened after heating in vacuo? It has been my experience that carburized tool steel parts will not always harden if heated in a neutral atmosphere and quenched. I have heated thousands of parts in as nearly a neutral atmosphere as can be obtained in a commercial practical way, that would not harden; the ferrite appeared under the surface of the steel in much the same way as is shown in the photomicrographs in this paper. The ferrite particles were very minute and occurred at, you might say, one grain deep; that is, there seemed to be numerous instances in the parts polished and etched in which the ferrite particles had a layer of steel over them that did not appear to be decarburized. I draw from this experience that it is necessary to harden tool steel in a reducing, or slightly reducing, atmosphere in order to obtain the proper results in a commercial way.

ZAY JEFFRIES,* Cleveland, Ohio.—I have never had much faith in the expulsion theory, as applied to changes in the solid state. We have

* Director of Research, Aluminum Castings Co.

much evidence supporting the elbowing action of insoluble materials during solidification, but in changes that take place wholly in the solid state, such as the changes around the A points in steel, I have not seen any evidence whatsoever that would lead one to suspect that a particle of slag or even a particle of cementite or any insoluble constituent in steel has been moved bodily by any of these transformations. On the other hand, there is considerable evidence showing practically no bodily movement in non-metallic materials, such as slag.

The grain growth of austenite, in the presence of a considerable portion of non-metallic material or other insoluble material, finds obstruction when the grain meets this material. That obstruction tends to force the stable grain boundaries to follow more or less the insoluble materials, but the grain boundaries are determined by the original positions of these insoluble constituents.

We may have argued the other way around, that the insoluble constituents, occurring oftentimes as they do at the grain boundaries, have been forced there but I believe that the grain boundaries owe their positions to the original positions of the non-metallic materals, or the other insoluble materials. There is a slight change in the non-metallic materials in these cases; that is, where one of these materials exists in the form of a plate or in any physical shape other than the spherical, at high temperature there is a tendency for these flattened out particles to change into more or less spherical shape; in that sense we do have bodily motion of the non-metallic or insoluble materials.

I have always attributed the concentration of ferrite and cementite at the austenite grain boundaries, during the cooling from the austenitic state to the region below the transformations, to more of a traction, or a tension, if we might call it that, the separation being initiated at the grain boundary, then impoverishing the austenite of the ferrite near the grain boundary. This solution of the austenite at the grain boundary causes a readjustment of the soluble carbon and thus draws the excess carbon to the grain boundaries.

J. W. Richards,* Bethlehem, Pa.—The paper bases the changes observed on the volatilization of the carbon from the surface of the specimen and states that it is not until the carbide dissolves in the iron as solution, above the A_1 point, that the carbon volatilizes; that at the same temperature the iron itself volatilizes less. It is perfectly true that carbon has a vapor tension at the temperatures worked with and so has iron; but from what we know of the vapor tensions, that of iron should be higher than that

* Professor of Metallurgy, Lehigh University.

of carbon; therefore, there appears to be a contradiction, and I do not understand why. Can any one suggest how carbon can volatilize faster at that temperature than iron, when the normal boiling point of carbon is about 3700° C. and that of iron about 2500°, showing that the carbon at this temperature would have considerably less vapor tension than the iron?

A New Occurrence of Pro-eutectoid Ferrite

By Charles Y. Clayton,* Met. E., Rolla, Mo.

(Lake Superior Meeting, August, 1920)

Cast-steel runners, while not interesting from a commercial standpoint, furnish valuable material for microscopic study. Foley[1] found not only the usual ingot structure, but zones of Widmannstättian structure, which he explains as due to differential crystallization. The writer, in examining nickel-steel runners, found a type of pro-eutectoid ferrite that is unusual and most probably new.

The runner in question was 8.75 cm. (3.5 in.) in diameter and analyzed at its center 2.69 per cent. nickel and 0.350 per cent. carbon and at its edge 2.62 per cent. nickel and 0.359 per cent. carbon. The macrostructure, which is the usual type, is shown in Figs. 1 and 2, which are a cross-section and the longitudinal surface, respectively. Slight segregation of ferrite can be seen near the center of the segment and at other points near the edges of polyhedral grains.

Stead's reagent brings out the dendritic structure within the grains as shown in Figs. 3 and 4. This texture is what would be expected of such a steel. Figs. 5 to 10 show the peculiar swirls of pro-eutectoid ferrite, the finding of which prompted this paper. These swirls, or eddies, if such a term can be applied, occur in all parts of the runner and in all parts of the individual grains. The upper left-hand figure shows this ferrite at a grain boundary; the middle left-hand figure shows the inner portion of a grain; and the lower left-hand figure shows these swirls at the edge of a grain which is also the outer edge of the runner.

Straight-lined ferrite associated with swirls is found in the areas of Figs. 11 and 12. The texture of the carbon-bearing constituent of the runner is shown to some extent in Fig. 12, the pearlite being very fine or sorbitic. Higher magnification does not bring out any new features either in the peculiar ferrite or in the pearlite. Figs. 13 and 14, at 240 diameters, show the curved and straight-lined ferrite.

* Associate Professor (in charge) of Metallurgy and Ore Dressing, Missouri School of Mines and Metallurgy.

[1] *Trans.* (1920) **62**, 347.

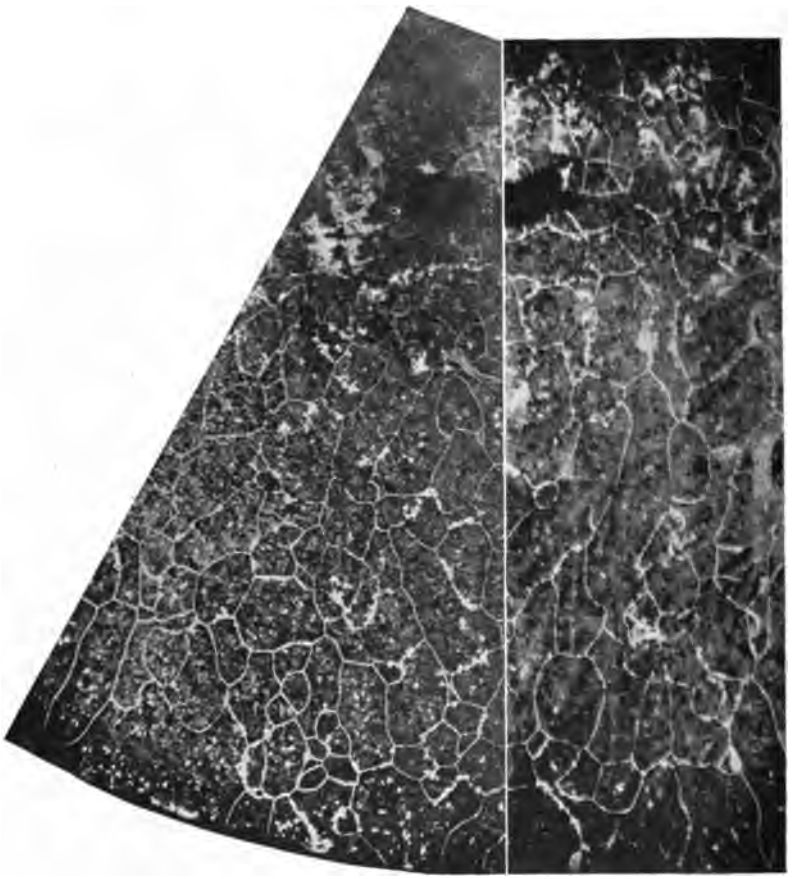


FIG. 1.—ETCHED WITH PICRIC ACID AND MAGNIFIED 3 DIAMETERS. SHOWS TYPICAL INGOT STRUCTURE. CROSS-SECTIONAL AREA.

FIG. 2.—ETCHED WITH PICRIC ACID AND MAGNIFIED 3 DIAMETERS. SHOWS AS IN FIG. 1, BUT IS LONGITUDINAL SURFACE.

FIG. 3.—ETCHED WITH STEAD'S REAGENT AND MAGNIFIED 3 DIAMETERS. SHOWS THE DISTRIBUTION OF PHOSPHORUS AND TYPICAL DENDRITIC STRUCTURE. SAME AREA AS IN FIG. 1.

FIG. 4.—ETCHED WITH STEAD'S REAGENT AND MAGNIFIED 3 DIAMETERS. SAME AREA AS IN FIG. 2.

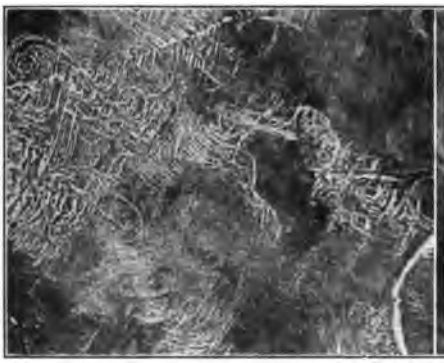


FIG. 5.

FIG. 6.

FIG. 7.

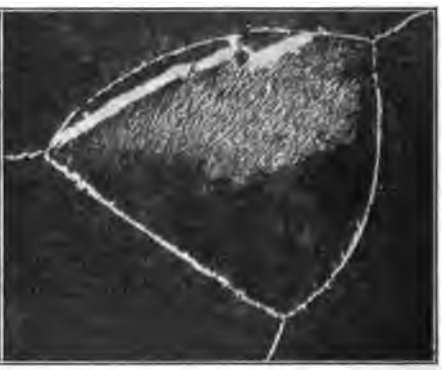


FIG. 8.

FIG. 9.

FIG. 10.

FIGS. 5, 6, 7, 8, 9, AND 10.—ETCHED WITH PICRIC ACID AND MAGNIFIED 60 DIAMETERS. SHOWS FERRITE WHITE AND SORBITE-PEARLITE DARK. THE SWIRLS OF FERRITE CAN BE SEEN IN A GROUNDMASS OF PEARLITE.

FIG. 11.—ETCHED WITH PICRIC ACID AND MAGNIFIED 120 DIAMETERS.

FIG. 12.—ETCHED WITH PICRIC ACID AND MAGNIFIED 120 DIAMETERS. STRAIGHT-LINED AND CURVED FERRITE IN EVIDENCE.

FIG. 13.—ETCHED WITH PICRIC ACID AND MAGNIFIED 240 DIAMETERS. SHOWS WIDMANNSTÄTTIAN TEXTURE AND SWIRLS OF FERRITE.

FIG. 14.—ETCHED WITH PICRIC ACID AND MAGNIFIED 240 DIAMETERS. SHOWS THREE ISOLATED SWIRLS OF FERRITE IN THE CENTER OF A GRAIN.

A possible explanation of these swirls of ferrite is that the whirling motion of the molten steel in the runner causes the tips of the dendrites and dendrite branches to be rounded at different periods of crystallization, due to resolution. Upon these rounded points, low-carbon austenite would be precipitated, due to selective freezing or the differential crystallization of Foley. Non-ferrous matter would, as a result, have a similar arrangement due to its stratigraphic history. Upon passage through the transformation range, the arrangement of the pro-eutectoid element would be dependent on the previous distribution of the ferrous and non-ferrous elements. Two cast nickel-steel runners from different heats exhibited this same peculiar occurrence of the pro-eutectoid element.

Acknowledgment is due the Minneapolis Station of the U. S. Bureau of Mines for its kind coöperation in making chemical analyses.

Graphitization of White Cast Iron

By R. S. Archer,* B. Ch. E., M. S., Cleveland, Ohio

(New York Meeting, February, 1920)

The proper representation of equilibria involving graphitic carbon in the constitutional diagram of the iron-carbon system is admittedly an unsolved problem, the complete solution of which will probably require the establishment of more experimental evidence than is at this time available. The object of this paper is to present the author's observations on some of the phenomena in question and his interpretation of this and other recorded evidence.

The chief of the recently disputed questions upon which the author has experimental evidence concerns the occurrence of graphitization at temperatures below the A_1 point. In a paper[1] presented at the September, 1919, meeting of this Institute, the following is found: "the results given would seem to indicate that the graphite eutectoid lies at a smaller value of carbon content than has been previously supposed. At least this is true unless there is either a marked formation of graphite eutectoid at these rates of cooling, or a decomposition of pearlite into graphite, both rather unlikely suppositions, but not impossible ones."

In a discussion of this paper, H. A. Schwartz[2] takes the position that the possibility of graphitization occurring below the A_1 point is an open question, but that complete graphitization (to less than 0.10 per cent. combined carbon) commonly occurs above this temperature.

Another opinion from the malleable castings industry is found in a recent paper[3] by Touceda: "Also the carbide of iron can be broken up into its two soft constituents at the temperature referred to. This temperature is called the critical temperature, or critical range, and for air-furnace hard-iron castings it is in the vicinity of 1440° F. It is the

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[1] P. D. Merica and L. J. Gurevich: Graphitization of White Cast Iron upon Annealing. *Trans.* (1920) **62**, 509.

[2] *Ibid.*, 518.

[3] Enrique Touceda: Research Work on Malleable Iron. *Jnl.* Amer. Soc. Mech. Engrs. (July, 1919).

lowest temperature at which hard-iron castings may be successfully annealed. This statement must be modified by the further statement that in an oven under perfect control this temperature is the one that would be selected. In practice, it would not be safe to adhere too closely to it, for the reason that should the castings while being held at temperature fall under the critical range, it would undo in large measure what had been accomplished above it." It is not certain that the "critical temperature" referred to is understood by Touceda to be the A_1 point of the iron-cementite system, but 1440° F. is certainly at or above the A_1 point of the hard-iron mentioned. It therefore seems to be his opinion that graphitization cannot be carried out below the A_1 point, and that heating a partly graphitized iron below this temperature will cause a reversal of the process.

The author questions the statements quoted and will try to show: (1) That graphitization can be initiated and completed (to less than 0.05 per cent. combined carbon) at temperatures below the A_1 point; (2) that complete graphitization is possible only at or below a point which is very close to, if not identical with, the A_1 point.

Practically all of the available evidence on graphitization concerns iron-carbon alloys rather high in silicon, since these are the most easily graphitized. It is therefore important to know the effect of silicon on the position of the A_1 point. Some determinations recorded in the literature are as follows:

Temperature of		Silicon Content, Per Cent.	Observers
Ar_1 Point, Degrees C.	Ac_1 Point, Degrees C.		
740–750		1.14	Wust and Petersen
730		0.97	Hague and Turner
734		1.19	Hague and Turner
700	815	1.1	Charpy and Cornu-Thénard

An unpublished curve taken in the laboratories of the General Motors Corpn. by C. Pfeifer gives 760° C. as the Ac_1 point for an iron containing 0.85 per cent. silicon. These results are all consistent, with the possible exception of those of Charpy. The latter suggest quite rapid heating and cooling in making the observations. The conclusion seems justified that the presence of 1.0 per cent. of silicon raises the Ac_1 point to at least 740° C. (1364° F.) and more probably to about 765° C. (1409° F.). Since graphitization is a slow process, the critical temperature in question is the A_1 point, which is generally considered to lie between Ar_1 and Ac_1, but much nearer to Ac_1. For a 1.0-per cent. silicon iron, A_1 is probably within 15° of 750° C.

In a previous paper,[4] rates of graphitization at various temperatures were given for a hard-iron containing 1.05 per cent. silicon. Two of the annealing treatments carried out for the determination of these rates are believed to have been conducted entirely below the A_1 point and there is no question that they produced complete graphitization. The mean temperatures were 690° C. and 735° C. and no deviations from these temperatures greater than 15° C. were observed during the heat treatments. The furnace used was not automatically controlled nor was a temperature recorder available. Therefore the following indirect evidence is submitted that the annealing temperatures remained below A_1. (1) Microscopic examination of every specimen of the two series showed that in all cases the pearlite was in the "divorced" state. This could not have been the case if the temperatures had oscillated about the A_1 point. (2) The results of experiments at 785° C. showed that at that temperature, which is not far above A_1, an annealing period of 10 hr. produced about 0.5 per cent. of graphitic carbon in this iron. In the 690° C. treatment, only 0.06 per cent. graphitic carbon was found after 24 hr. The progress of graphitization during the 690° C. and 735° C. treatments is shown in Table 1.

TABLE 1.—*Progress of Graphitization*

Test No.	Annealing Temperature	Time at Heat, Hours	Total Carbon, Per Cent.	Graphitic Carbon, Per Cent.	Combined Carbon, Per Cent.
D-1	690° C. (1274° F.)	24	2.89	0.06	2.83
D-2	690° C. (1274° F.)	47	2.75	0.47	2.28
D-3	690° C. (1274° F.)	75	2.87	1.31	1.56
D-4	690° C. (1274° F.)	95	2.87	1.82	1.05
D-5	690° C. (1274° F.)	119	2.80	2.33	0.47
D-6	690° C. (1274° F.)	149	2.77	2.49	0.28
D-7	690° C. (1274° F.)	168	2.75	2.70	0.05
D-8	690° C. (1274° F.)	193	2.68	2.68	None
D-9	690° C. (1274° F.)	221	2.76	2.75	None
C-1	735° C. (1355° F.)	11	2.92	0.12	2.80
C-2	735° C. (1355° F.)	24	2.90	0.39	2.51
C-3	735° C. (1355° F.)	37	2.93	1.27	1.66
C-4	735° C. (1355° F.)	48	2.78	1.83	0.95
C-5	735° C. (1355° F.)	60	2.74	2.05	0.69
C-6	735° C. (1355° F.)	72	2.74	2.31	0.43
C-7	735° C. (1355° F.)	84	2.76	2.42	0.34
C-8	735° C. (1355° F.)	96	2.68	2.50	0.18
C-9	735° C. (1355° F.)	120	2.58	2.51	0.07
C-10	735° C. (1355° F.)	150	2.56	2.51	0.05

[4] A. E. White and R. S. Archer: The Annealing of Malleable Castings. *Trans.* Am. Foundrymen's Assn. (1918).

The material used for these experiments was a lot of hard-iron bars ⅜ in. square cast from a single ladle of metal in a green-sand mold. The analysis was: Total carbon, 2.90 per cent.; graphitic carbon, none; silicon, 1.05 per cent.; manganese, 0.35 per cent.; sulfur, 0.035 per cent.; phosphorus, 0.11 per cent. The test pieces were heated in a wire-wound electric furnace and due precautions were taken that the temperatures indicated were correct and represented the actual temperatures of the test pieces. The furnace chamber was filled with charcoal but not in contact with the test pieces. This resulted in fairly satisfactory protection from decarburization, and microscopic examination showed that in no case was a ferrite rim formed. After the specified periods of annealing, the specimens were removed from the furnace and dropped into a box of ashes. The time of cooling from the annealing temperature to below a red heat did not exceed 20 min. Opposite sides of the test pieces were ground down about $\frac{1}{32}$ in. and drillings taken for analysis, the drill passing through the test piece. From these drillings samples were taken by the parting method. The samples for total carbon were not screened. Both total and graphitic carbons were determined by combustion.

A different line of evidence concerning the temperature ranges of graphitization is furnished by reheating a completely graphitized iron. Specimens were prepared from a malleable test bar in the form of cylinders ⅝ in. in diameter by 1 in. in length. A ⅛-in. hole was drilled down the axis of the specimens to a depth of ½ in. A thermocouple, especially checked for the purpose, was packed into this hole with asbestos, which insulated the wires of the couple from the sides of the hole and from each other. The specimen was then heated to a specified temperature, the rate of heating being quite slow as the temperature was approached. The specimen was held at this heat for 15 min. and then cooled in air.

The structures of two such specimens are shown in Figs. 1 and 2. Both are etched in an alcoholic solution of picric acid and magnified 100 times. It will be noted that the specimen reheated to 749° C. (1380° F.) shows no combined carbon, while the one heated to 771° C. (1420° F.) does show combined carbon. It was not considered necessary to analyze this material. This reversion of graphitic carbon to combined carbon has been observed and recorded by Touceda, who found no combined carbon on reheating to 760° C. but did after heating to 788° C. A similar observation is reported by Storey and Leasman.

It therefore appears to be a well-established fact that there is a temperature above which the graphite of a completely graphitized iron will go back into solution, to be reprecipitated as iron carbide on cooling. For iron of the composition used for malleable castings (0.5 to 1.0 per cent. silicon) this temperature is approximately 765° C. The conclusion seems inevitable that combined carbon cannot be completely converted

to graphitic carbon under conditions that cause graphitic carbon previously formed to revert to dissolved carbon and, on moderately rapid cooling, to cementite. That is, it is not possible above this critical tem-

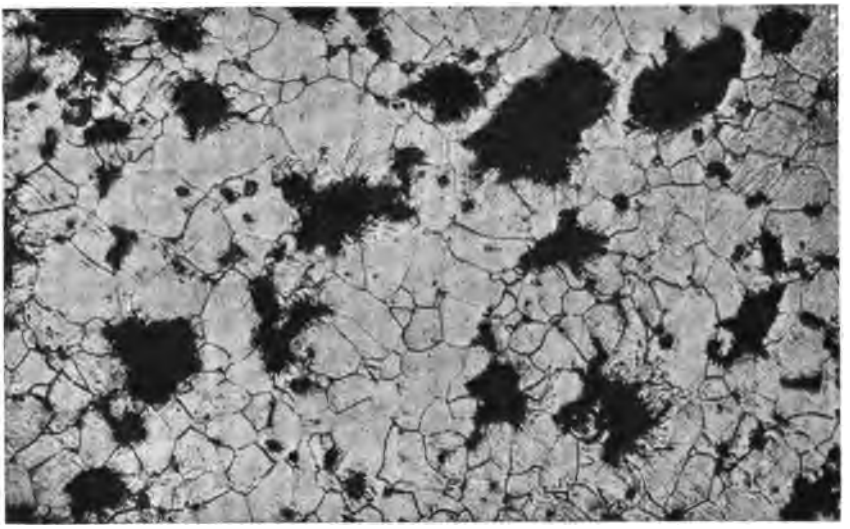


FIG. 1.—REHEATED TO 749° C.

FIG. 2.—REHEATED TO 771° C.

perature to convert combined carbon completely to graphitic carbon. If this is true, it follows that the complete conversion regularly obtained in properly annealed malleable castings must, of necessity, take place in its final stages either at or below this critical temperature.

Graphite versus Carbide Equilibrium

Whether the completion of graphitization takes place at or below a definite critical temperature is a question of importance. If, as maintained by some of the writers quoted, the complete conversion to graphite takes place at this critical temperature and not below it, such conversion must consist in the direct precipitation of an iron-graphite eutectoid. For if the conversion took place simultaneously with the formation of pearlite, there is no reason to suppose that it would not continue at temperatures slightly below the critical.

Table 2.—*Solubility of Graphite in Iron*

Test No.	Annealing Temperature	Time at Heat, Hours	Total Carbon, Per Cent.	Graphitic Carbon, Per Cent.	Combined Carbon, Per Cent.
F-1	835° C. (1535° F.)	5	2.87	0.54	2.33
F-2	835° C. (1535° F.)	9	2.83	1.41	1.42
F-3	835° C. (1535° F.)	19	2.80	1.96	0.84
F-4	835° C. (1535° F.)	24	2.76	1.93	0.83
E-1	785° C. (1445° F.)	41	2.76	1.76	1.00
E-2	785° C. (1445° F.)	45	2.80	1.87	0.93
E-3	785° C. (1445° F.)	50	2.72	1.96	0.76
E-4	785° C. (1445° F.)	55	2.73	2.07	0.66
E-5	785° C. (1445° F.)	65	2.75	2.07	0.68

When white cast iron is heated sufficiently long at temperatures above 785° C., the combined carbon content reaches a constant value for any given temperature. It has been well established that these values increase with the temperature. It is by plotting such values against the temperatures of annealing that the solubility curve of pro-eutectoid graphite has been obtained.[5] This curve, as Desch remarks, is suspiciously close to the solubility curve for cementite. The author suggests that the solubility curve of graphite can, for practical purposes, be considered to be identical with that of cementite, if due allowance is made for the effect of silicon on the solubility of cementite, and on the temperature of the A_1 change. In the experiments referred to above to determine rates of annealing, some evidence was obtained as to the solubility of graphite in iron containing 1.05 per cent. silicon at temperatures just above A_1.

The method of cooling after the annealing period seriously affects the results of such experiments. The test pieces of set *F* were air-cooled

[5] *Trans.* (1920) **62**, 516.

after withdrawing from the furnace. A piece similarly treated but quenched showed a combined carbon content of 0.86 per cent. This may indicate a slight additional precipitation of graphite during air-cooling, but the difference is within the errors of analysis. Another test piece was cooled from the same temperature under ashes, as described; the combined carbon content was then 0.67 per cent. This shows that the short time occupied in passing through Ar_1 and through temperatures immediately below Ar_1 was sufficient to allow the formation of nearly 0.2 per cent. more graphitic carbon. It is thought that the sensitiveness of such material to slight changes in the cooling rate has not been sufficiently appreciated, and that this accounts for some apparently inconsistent results in the literature.

As stated before, the test pieces of set *F*, after air-cooling and after quenching gave consistent results, so that the value 0.85 per cent. is considered to be a reliable figure for the solubility of graphite at 835° C., in the presence of 1.05 per cent. silicon. The test pieces of set *E*, however, were cooled under ashes, so that the results only show the solubility at 785° C. to be between 0.66 and 0.85 per cent. Since this temperature is only slightly above A_1 (assumed to be at 765° C.), it is thought that this evidence points to a eutectoid composition in good agreement with that given by Guertler (0.70 per cent.).

When allowances are made for the chemical effect of silicon and phosphorus and for the bulk effect of graphite on the composition of the pearlite eutectoid, it is the author's opinion that 0.70 per cent. carbon is so close to the value to be expected that the iron-cementite and iron-graphite eutectoids may be considered as practically identical.

Summary

Evidence is submitted which is thought to demonstrate two facts. That graphitization can be initiated and completed in a white cast iron at temperatures below the A_1 point; and that graphitization cannot be completed at temperatures above a point which is very close to and perhaps identical with the A_1 point.

It is suggested that the phenomena of graphitization are in satisfactory agreement with the following general statements:

1. With the possible exception of the initial stages, graphitization takes place directly from solid solution.

2. Graphitization may take place from any solid solution supersatutated with respect to graphitic carbon.

3. The evidence at present available is not sufficient to determine whether the saturation values for a solid solution on the point of precipirating graphite are appreciably different from those for a solid solution

on the point of precipitating cementite. Under conditions of equilibrium, two phases are present—graphitic carbon and the saturated solid solution. Metastable equilibrium may exist between the two phases iron carbide and solid solution. Theory indicates that the carbon concentration of solutions in stable equilibrium with graphite is less than that of solutions in metastable equilibrium with iron carbide. If the available experimental evidence is considered with allowance for the effect of impurities on the solubility of iron carbide, the solubility curve of the carbide may, for practical purposes, be used to determine the conditions of equilibrium in the stable system iron graphite.

DISCUSSION

A. E. WHITE,* Ann Arbor, Mich.—The author has called attention to a matter relating to the constitution of iron and graphitic carbon that has received too little attention in recent years. When the various opinions concerning the equilibrium between iron and graphitic carbon come into closer agreement, we may expect to see the foundryman's profession become more of a science than it is today. There is nothing new or strange in the belief that graphite should precipitate at temperatures below the critical. The normal state of equilibrium for iron and carbon, at temperatures below the critical, is free iron and free graphite. When the time, temperature, and composition conditions are such that equilibrium is not effected, it is not because the tendency to reach equilibrium is not there, but because certain conditions have not been attained. For example, suppose that it is necessary to hold an iron of a given composition for 193 hr. at 690° C. (1274° F.), in order to convert all the carbon from the combined to the graphitic state and that 600 hr. is necessary to effect complete conversion at 690° C. $- X°$. The only predetermined change in the two conditions is that the temperature in the second case is lower than in the first, with the result that a longer time for the annealing is necessary. One does not need to go much below 500° C. (932° F.) before the time necessary for complete conversion would be so long that the normal three score years and ten alloted to man would be insufficient to observe complete conversion. It is quite possible that at the low temperatures the metal would not be sufficiently mobile to permit the conversion to go to completion under any condition of time. These conditions are barriers to conversion though they do not remove the tendency for conversion.

At temperatures above the critical, equilibrium calls for graphite and solid solution. This means that on analyzing a piece of metal that has reached equilibrium at a given temperature above the critical, the carbon will be in both the combined and the graphitic states. Further,

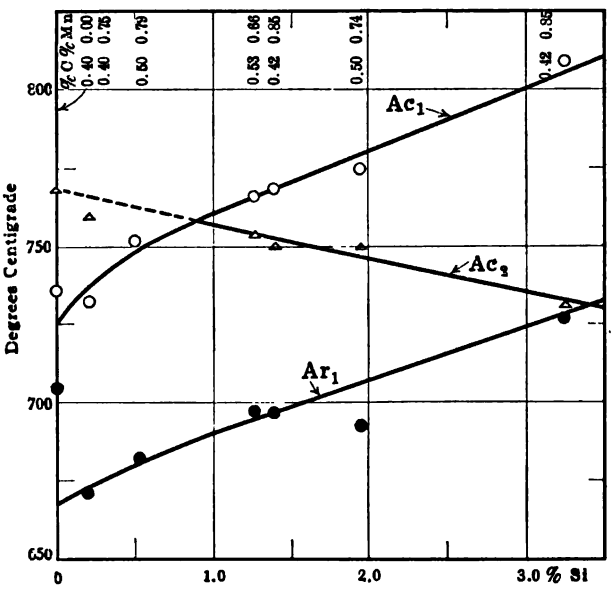
* Professor of Chemical Engineering, University of Michigan.

the higher the temperature above the critical, the greater will be the amount of carbon held in solution. Both Mr. Touceda and Messrs. Merica and Gurevich have shown this to be true.

Mr. Archer states that he assumes the critical temperatures of the iron he is discussing to be between 740° C. (1364° F.) and 765° C. (1409° F.). It may be of interest to note that the critical temperature of one of the irons used in the investigations set forth in this paper showed that the *Ar* temperature was 771° C. (1420° F.), the *Ac* temperature was 737° C. (1360° F.) with a mean of 754° C. (1390° F.). On another sample of good standard malleable, the *Ac* was 782° C. (1440° F.), the *Ar* 743° C. (1370° F.), and the mean was 762° C. (1405° F.).

The writer agrees with Mr. Archer that the proper representation of equilibriums involving graphitic carbon in the constitutional diagram of the iron-carbon system is admittedly an unsolved problem. Work is being done and it is hoped that in the not too distant future there may be more experimental evidence on the questions at issue.

HOWARD SCOTT,* Washington, D. C.—I get practically the same temperature as Mr. White for Ac_1 and a little lower for Ar_1. The accompany-



ing chart shows the results obtained for 0.50-per cent. carbon steels.

Mr. Archer's paper indicates that the graphite forms directly from the free cementite. If that is the case, it explains many things. It gives a clue to the effect of silicon in promoting graphitization. Silicon

* Assistant Physicist, U. S. Bureau of Standards.

raises the critical points, and therefore the iron has more cementite exposed, in the form of pearlite, at a higher temperature where the rate of graphitization is greater and consequently a larger quantity of graphite will be formed in the same time; that is not the only effect of silicon in iron, but at least it is one of the effects. It explains, also, why it is so difficult to obtain graphite in steel. When steel is heated above the critical point, practically all of the cementite is in solution. If graphite does not form from solid solution, graphitization cannot very well be started in the most effective temperature region, but must be confined to the less effective one below A_1.

O. W. STOREY, Madison, Wis. (written discussion).—Mr. Archer, in general, confirms the results and deductions at which I arrived several years ago during a lengthy unfinished research on malleable iron.[6] The composition of the white iron used in my work was as follows: Total (combined) carbon, 2.60 to 2.70 per cent.; silicon, 0.65 to 0.70 per cent.; sulfur, 0.055 to 0.060 per cent.; phosphorus, 0.140 per cent.; manganese, 0.27 per cent.

Mr. Archer shows that the white iron may be malleableized at 690° C., provided it is held at that temperature for a sufficient length of time; in the case cited, this is about 150 hr. I found that annealing at 700° C. for 50 hr. produced specimens that were slightly malleableized but too hard to saw. Specimens annealed at 730° C. for 50 hr. were sawed with difficulty. However, specimens annealed at from 535° to 650° C. for 120 hr. were too hard to saw and gave no indications of being even slightly annealed; unfortunately, a microscopic examination was not made. On the whole, the results check closely.

At that time, my microscopic investigations led me to state that graphitization apparently takes place from solid solution, which conclusion is also reached by Mr. Archer. However, in studying Mr. Archer's data, several questions have arisen which will need explanation before I can accept this conclusion.

It is shown that the average point for this particular white iron is about 750° to 765° C. Above this temperature, the pearlitic iron carbide is in solid solution while below this temperature the carbon is entirely in the form of carbide; that is, the carbon in the form of cementite is completely insoluble in the ferrite. Mr. Archer has demonstrated that complete malleableization may be secured at 690° C. and his photomicrographs show an excellent structure of temper carbon in ferrite. If the Ar_1 point is above 750° C., this experiment would seem to show conclusively that graphitization does not need to take place from a solid solution. Is the assumption that the Ar_1 point is at 750° C. incorrect?

[6] *Met. & Chem. Eng.* (June, 1914) **12**, 383; *Trans.* Amer. Foundrymen's Assn (1915) **23**, 460.

Is there a limited solubility of iron carbide in ferrite below the Ar_1 point, keeping in mind that we are not dealing with pure iron but one that contains several impurities?

If we assume that there is a total insolubility of iron carbide in ferrite, we must assume that the ferrite at 690° C. is sufficiently mobile to allow a rather free migration of iron carbide or graphite to the temper-carbon nuclei. This does not seem possible to me. When I reached my conclusion of the graphitization from solid solution, I did not have a 750° Ar_1 point to worry about as I assumed the Ar_1 point to be at 670° to 700°. The following data would seem to show that graphitization does not take place below 670° to 700°.

Samples of malleable iron were first heated to 900° C. for 5 min. to insure the solution of a large proportion of temper carbon. The specimens were then cooled to temperatures ranging from 650° to 800° C. and kept at these temperatures for varying lengths of time. Specimens heated at 700° to 775° C. for from 4 to 5 hr. showed a structure like the original malleable; that is, temper carbon and ferrite. Specimens heated at 650° and 675° C. did not show traces of a breakdown even when annealed for 6 hr. In another experiment, some white iron was annealed at 875° C. for 50 hr. One specimen was cooled quickly to 750° C. and kept at this temperature for 10 hr. The second specimen was cooled quickly to 650° C. and kept at this temperature for 20 hr. The first specimen gave an excellent malleable structure while the second was brittle and steely in appearance. Similar experiments were carried out with gray cast iron. Some specimens of unknown composition were heated at 700°, 750°, and 800° C. for several hours. The pearlite was broken down completely. No decomposition could be obtained if the temperature was much below 700° C.

A striking point is the rapidity with which temper carbon goes into solution if malleable iron is heated above 800° C. By heating specimens for 2 hr. at 800°C., a small amount (estimated at 0.25 per cent.) of carbon went into solution. By heating at 850° C. for 5 min., the entire specimen consisted of pearlite and temper carbon and was brittle.

A study of the data shows that there is a dearth of data on low-temperature malleableizing. The lower limits have not been established and there is doubt as to the actual process by which the iron carbide decomposes at these low temperatures. If it can be proved that a solid solution exists at these temperatures and that the Ar_1 point is below 700° C., the solution is simple. However, if this temperature is above 700° C., another explanation must be sought. The high temperature for the Ar_1 point given is surprising in view of Guillet's work, which shows that silicon has no effect on the critical points.

J. W. RICHARDS, CHAIRMAN, Bethlehem, Pa.—Mr. Scott's diagram, showing that silicon raises the critical point, is a direct contradiction of

the last statement of Mr. Storey's discussion. If silicon raises the critical points and the critical points are really brought up to the temperatures shown by Mr. Scott, the explanation brought forth by Mr. Archer is the more likely one and Mr. Storey's criticisms are without foundation.

J. V. EMMONS,* Cleveland, Ohio.—Being a tool-steel user, my interest in graphitization lies in preventing it, while Mr. Archer's lies in producing it; however, the chemical reactions are the same. I confirm the statement that graphitization can, and does, take place below the critical range; that has been shown conclusively in tool-steel work. But I cannot agree with the statement that graphitization takes place preferably from the solid solution. Conclusive experiments show that graphitization proceeds at a very rapid rate at temperatures below the Ar_1 point, below which point I do not believe that a solid solution exists in annealed steels and that the graphitization is proceeding directly from the cementite.

S. L. HOYT,† Cleveland, Ohio.—Was the steel in which the graphitization occurred below the critical point annealed steel, or a heat-treated steel?

J. V. EMMONS.—Annealed steel.

S. L. HOYT.—That is, an annealed steel with the cementite precipitated out of it.

LEONARD WALDO, New York, N. Y.—Is there any knowledge of the graphitization at extremely low temperatures, even though over long periods of time and to a slight degree? By long periods of time I mean days or weeks; and by low temperatures, temperatures approximating the boiling point of water, say 100° C., or something of that kind.

R. S. ARCHER.—The question as to whether graphitization takes place directly from the solid solution has only been touched on in the paper, but since it has come up, I would like to give reasons for my opinion. The most definite evidence is the common observation of graphite particles surrounded by a rim of ferrite, which is in turn surrounded by pearlite. I do not see how the graphite can get to that nucleus unless it goes through the ferrite. As to the objection raised that carbon is insoluble in ferrite, I think it is relatively insoluble as compared to its solubility in austenite, but that there is no such thing as absolute insolubility.

The graphite nucleus, which has been referred to as a globule, is not at all solid. These particles of graphite, like the flakes of graphite

* Metallurgical Engineer, Cleveland Twist Drill Co.
† Metallurgical Engineer, Nela Park.

observed in gray iron, are more or less laminated. Because of the softness of these areas, they are worn down below the surface of the metal during the polishing and the laminations are usually not observed. Occasionally, however, areas are found where the polishing is satisfactory and with a microscope the laminations of ferrite can be clearly seen.

The formation of graphite directly in the position previously occupied by cementite, which was observed by Mr. Emmons, is in accordance with the exception which I made in the statement that graphitization takes place directly from the solid solution with the possible exceptions of the initial stages. It is probable that when no graphite nuclei are present, the particles of cementite become the most favorable points for the beginning of graphitization.

The effect of silicon comes in more directly from the formation of iron-carbon-silicon compounds. W. H. Hatfield, in his book "Cast Iron in the Light of Recent Research," shows that the carbides in cast iron contain silicon.

ENRIQUE TOUCEDA, Albany, N. Y. (written discussion).—It might not be amiss to explain that the paper to which Mr. Archer refers was prepared at the request of the Research Committee of the American Society of Mechanical Engineers as one of a series of popularly written papers by various authors for the purpose of showing the broad application and commercial value of such work to manufacturers in general, in order to excite and stimulate their interest in this direction. The paper was prepared with this end in view and not with the object of entering into an academic discussion of research details.

The writer believes that while Mr. Archer has been perfectly honest in his attempt to interpret the writer's meaning in that part of the text he has quoted, he has failed to appreciate the fact that the writer was basing his remarks on conditions that must exist in commercial practice, and not on a hard-iron composition of the character selected by Mr. Archer for his experiments. In short, the writer's remarks were confined to air-furnace hard-irons which, when properly annealed, will produce castings that are of high ultimate strength and ductility, accompanied by machining characteristics that will make possible their being tooled on automatics run at almost brass-cutting speed.

While the writer may be in error, he believes that Mr. Archer is not familiar with the practical requirements of malleable-iron castings, or with their commercial manufacture; otherwise Mr. Archer would not have selected for his experiments a hard-iron having a silicon and carbon content of 1.05 per cent. and 2.90 per cent., respectively, when he could have more easily obtained from some manufacturers bars of a representative composition. The writer is surprised to learn that Mr. Archer found samples, even as small in section as are his bars, free from graphitic

carbon; such hard iron when annealed will produce a casting whose ultimate strength and ductility will be far under specification requirements, and consequently would not be commercial.

Mr. Archer correctly repeats the well known fact that iron-carbon alloys high in silicon are most easily graphitized, but why does he ignore the carbon content, which in this particular has a more marked effect, in the writer's opinion? Inasmuch as it has been demonstrated that the lower the carbon in the air-furnace hard iron, the higher is the combined ultimate strength and elongation when annealed, it is the practice, in the manufacture of malleable castings, to make an air-furnace mixture such as will produce a hard iron that will average perhaps 2.30-per cent. carbon, and will run at times as low as 2.00 per cent; or, expressed in other words, a carbon content as low as will not prevent complete graphitization in regular annealing practice nor be so low as to lessen the fluidity of the iron to a point where misruns will be excessive. The remarks of the writer were confined to this character of hard iron and not to one that, by virtue not only of high silicon but with a carbon content so high that it will graphitize with great ease, is permissible in cases only where neither strength nor ductility is a factor. Such a composition as was selected by Mr. Archer can be graphitized with great facility and will be very fluid, but when annealed it will produce worthless material, compared with the character of castings produced today; its use must, of necessity, be restricted to exceedingly thin castings in order to avoid the presence of primary graphite in the hard iron. Had Mr. Archer conducted the same experiments with a 2.25-per cent. carbon hard iron he would have found the time required for complete graphitization considerably longer than those in his table.

Referring to the writer, Mr. Archer says: "It therefore seems to be his opinion that graphitization cannot be carried out below the A_1 point, and that heating a partly graphitized iron below this temperature will cause a reversal of the process." As has been explained, the writer in his paper had in mind commercial practice only. According to Table 1 of Mr. Archer's paper, it took practically 8 days to bring about complete graphitization in sample D–8 at a temperature of 1274° F., while it took 6¼ days at 1355° F. to graphitize sample C–10, which contained 0.05 per cent. of combined carbon at the end of this period. In commercial practice it is unnecessary to hold the ovens "at temperature" longer than 60 hr., and in many cases only 48 hr. If Mr. Archer had said "It therefore seems to be his opinion that graphitization cannot be carried out (commercially) below the A_1 point" he would have correctly expressed the thought that was in the writer's mind at the time and which he wishes to make plain now.

The writer did not mean that if graphitization had progressed in part, or almost to completeness, and the temperature had fallen below

the critical point, to be subsequently raised to the annealing temperature for the length of time that past experiences indicated was sufficiently long for complete graphitization, all of the previous graphitization would be destroyed, but he has reason to believe that a considerable amount of the temper carbon that had formed would recombine, unless the period at which the castings were held "at temperature" was lengthened beyond that regularly found sufficient when no oscillations occurred. In such a case, the ground mass of the castings would be found to contain considerable pearlite, which means that these castings would be returned by the purchaser as being too hard to machine.

The manufacturers of malleable cast iron would welcome any practical scheme that would enable them to anneal their castings at a lower temperature than has been recommended by the writer, for it would increase the life of their annealing pots and would effect a saving in fuel, as well as in maintenance, provided the length of time of anneal was not increased.

Mr. Archer must keep in mind: first, that it is one thing to anneal a piece of white iron of $\frac{3}{8}$-in. section, and quite another to anneal uniformly castings in ovens of 30 to 60 tons capacity; second, complete graphitization is only part of the story, for this can be accomplished and still the material can be worthless.

The writer has been conducting some experiments in connection with several phases of graphitization, and at the conclusion of the work will submit a paper on this subject. The writer is very glad to have the data presented by Mr. Archer, and would welcome similar data on white irons of a silicon-carbon content of approximately 0.90 per cent. and 2.25 per cent. respectively.

H. A. SCHWARTZ,* Indianapolis, Ind. (written discussion).—The author has presented experimental data calculated to advance our knowledge on this point. The writer is, however, unaware of any reason why Archer should quote him as believing that graphitization is commonly complete above A_1. He has specifically described the locus of the solubility of free carbon on the equilibrium diagram[7] as intersecting the line of zero carbon concentration at about 680° C. Whether or not this opinion is well founded, it amounts to a statement of his belief that graphitization is incomplete at all temperatures above this point. This temperature, whatever it may be, is the critical point referred to[8] as being near to but probably below A_1 of the metastabile system.

It is quite possible that temperatures below such a critical point will

* Metallurgical Engineer, The National Malleable Castings Co.

[7] *Trans.* (1920) **62**, 521.

[8] *Op. cit.*, 519.

furnish sufficient freedom to permit the conversion of the metastabile into the stabile system. If this freedom did not exist at A_1 of the stabile system, the complete graphitization of white iron would be impossible. Just how far below A_1 of the stabile system graphitization can be initiated or maintained is not known to the writer. Consideration of all the available information seems, however, to point to the fact that graphitization can at least be maintained, and possibly initiated, at temperatures materially under A_1 of the stabile system, and hence under A_1 of the metastabile system.

Bean[9] has published graphs showing Ar_1 for malleable cast iron to be at 727° C., while Ar_1 for the corresponding white cast iron was 746° C. This points to a higher value of Ar_1 (stabile system) than that previously assumed by the writer and a lower one than that assumed by Archer. It is still in accord with the writer's original view that the critical point of the stabile system is near but below that for the metastabile.

Archer differs from the writer in assuming that the solubility of carbon falls to a value roughly 0.65 per cent. just at Ar_1 and to zero on passing below Ar_1. The writer's provisional opinion had been that the solubility fell gradually to zero at Ar_1. The two views are shown in the accompanying diagram.

It will be noted that apparently Archer's conclusions are supported about as well by his data as the writer's are by his own. Both are based on assumption as to the location of Ar_1 in the stabile system. It would be very well if the experiments had included a determination of this point on the identical metal under observation; this deficiency can be supplied later on the writer's material.

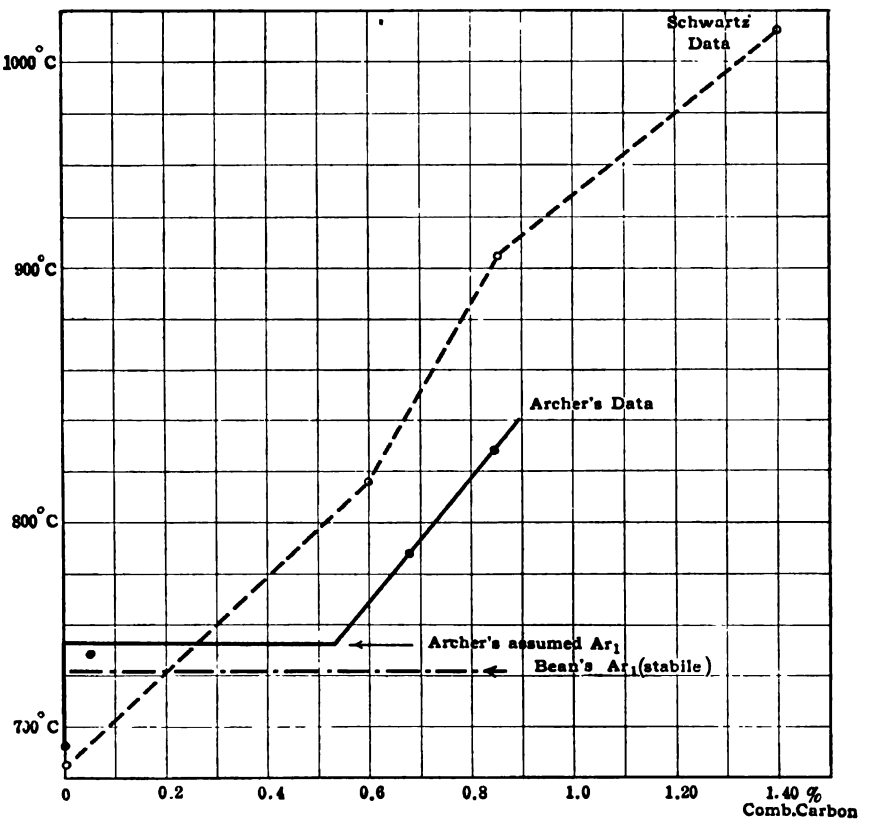
If Bean's figure is correct, Archer's *C* series is just above Ar_1 (stabile system) instead of just below. In that case his result C–10, instead of pointing to a slightly incomplete attainment of equilibrium points to a slight solubility of carbon and confirms the writer's view that the solubility falls nearly uniformly as Ar_1 is approached and reaches zero at that point.

It is interesting to note the probability that if Ar_1 stabile is above 680° C., as it probably is, the eutectoid composition can be determined from the writer's figures only by extrapolation from the data at high temperatures. In the regrettable absence of a determination just over Ar_1, this cannot be done with accuracy, especially since the three higher points do not fall on a straight line. Archer's figures, showing only two determinations reasonably above Ar_1 cannot be checked up as to their probable accuracy from this viewpoint. If his *C* series is below Ar_1 the results are not comparable with *E* and *F*; if above, as indicated by Bean, the *C* series does not confirm *E* and *F*. The data of Archer's *C* series

[9] *Jnl.* Amer. Soc. Test. Mat. (1919) **19**, Pt. 2.

would fit fairly well as the termination of the writer's if it were just above Ar_1 stabile.

As the situation stands, it is admitted by all that Ar_1 (stabile) must be below Ar_1 (metastabile) by an unknown amount; that the solubility of carbon (stabile) must be less than the solubility of carbon (metastabile) at any given temperature. Archer believes with Guertler that graphiti-



COMPARISON OF ARCHER'S DATA WITH SCHWARTZ' ON THE SOLUBILITY OF CARBON, STABILE DIAGRAM.

zation is completed in passing through Ar_1 (stabile) by the precipitation of an iron-carbon eutectoid containing approximately 0.70 per cent. carbon and, therefore, but slightly to the left of the iron-cementite eutectoid pearlite. The writer supports Merica in the thought that the alloy reaches Ar_1 very low in combined carbon, probably indefinitely near zero.

Every one agrees that ferrite will be found only below Ar_1 (stabile). The writer has repeatedly observed, microscopically, the completion of graphitization at temperatures below Ar_1 (metastabile) and presumably below Ar_1 (stabile) by the progressive conversion of pearlite into temper

carbon and ferrite. This has always occurred in circumstances where the cooling to Ar_1 (metastabile) was too rapid to permit of much graphitization during the cooling; hence, presumably, the solid solution was supersaturated, as it were, with carbon on reaching Ar_1 and deposited pearlite. It is a matter of considerable industrial importance whether graphitization is always completed by the precipitation of a eutectoid or is completed by the progressive graphitization of a solid solution.

The writer has invariably found that reheating a graphitized metal to a given temperature produces a higher combined carbon concentration than that corresponding to the termination of the graphitizing reaction. The results are as follows:

Temp., Degrees C.	$3Fe+C \rightarrow Fe_3C$ Per Cent., Carbon	$Fe_3C \rightarrow 3Fe+C$ Per Cent., Carbon	Temp., Degrees C.	$3Fe+C \rightarrow Fe_3C$, Per Cent., Carbon	$Fe_3C \rightarrow 3Fe+C$, Per Cent., Carbon
680	....	0.00	930	....	0.85
767	0.20	....	985	1.60	....
820	....	0.60	1040	....	1.4
875	1.50	....	1090	1.7	....

The data for the reaction $3Fe+C \rightarrow Fe_3C$ bear a resemblance to the cementite solubility line but are to the right of that line. The data $Fe_3C \rightarrow 3Fe+C$ are those used by the writer in developing his views as to the solubility of graphite. There appears to be urgent need for a long series of observations at temperatures extending from well above Ar to moderately below that point, which also must be definitely determined on the metal being used.

R. S. ARCHER (author's reply to discussion).—The discussion has furnished abundant evidence confirming the fact that graphitization can be initiated and completed below the Ae_1 temperature of the metastable system. Mr. Emmons and Mr. Schwartz have reported direct observation of the graphitization of pearlite, while the data of Prof. A. E. White and Mr. Scott show the Ae_1 temperature of the iron used in my experiments to be well above the annealing temperatures employed in series "C" and "D."

It is interesting to calculate the critical temperatures of cast irons of different silicon content from the data given by Mr. Scott. Because of the slow heating and cooling involved in processes of graphitization, the critical temperature with which we are concerned is Ae_1 rather than Ac_1 or Ar_1. Doctor Howe has given 725° C. as the Ae_1 temperature of the pure iron-carbon system.[10] Mr. Scott shows that silicon raises the Ac_1 and Ar_1 temperatures at substantially linear rates, at least up to 3 per cent. silicon. The average increase of Ac_1 for 1 per cent. of silicon is 25° C. while Ar_1 is raised 19° C. One per cent. of silicon may, therefore,

[10] *Trans.* (1913), **47**, 647, 743.

be considered to raise the Ae_1 approximately 22° C. The critical temperature of any cast iron fairly low in impurities is then expressed by the equation:

$$Ae_1 = 725 + 22 \times \text{per cent. silicon.}$$

On this basis the critical temperature of the iron which I used is 748° C. Applying the same formula to Mr. Storey's iron, 740° C. is obtained as the critical temperature; his experiments, therefore, confirm the graphitization below Ae_1.

The question of the mechanism of graphitization, raised both by Mr. Storey and Mr. Emmons, was considered in the oral discussion.

Mr. Scott suggested that the effect of silicon in promoting graphitization is due, in part at least, to the raising of the A_1 temperature. This is undoubtedly a factor in the case of hypereutectoid steels. In white irons, at all temperatures, the solid-solution phase is saturated with iron carbide and plenty of structurally free carbide is present to act as centers for graphitization. Silicon influences the rate of graphitization, which must be due to something other than its effect on the critical temperature.

Mr. Touceda corrects my misinterpretation of his statements in a previous paper; that graphitization cannot be carried out commercially below the A_1 point. With this statement I agree, if he means complete graphitization. The last stages of graphitization, say from 0.70 per cent. combined carbon down to the traces left in good malleable castings, can only be carried out at or below the critical temperatures; in the commercial annealing of malleable castings, the larger part of this 0.70 per cent. combined carbon is graphitized below the critical temperature. He has unnecessarily complicated his discussion by introducing consideration of the commercial quality of the iron used in my experiments. The facts of chemical equilibrium, which alone were under discussion, are not influenced by the tensile properties of the finished product nor by the size of the annealing furnace. Since the point has been raised, however, it may be well to state that the iron I used was taken, in the summer of 1916, from the regular run of a foundry having a large production of malleable castings for the automobile trade, and that test bars cast at the same time and annealed in the foundry ovens passed the A.S.T.M. specifications of that time.

In the eighth paragraph of his discussion, Mr. Schwartz says: "As the situation stands, it is admitted by all that Ar_1 (stable) must be below Ar_1 (metastable) by an unknown amount; that the solubility of carbon (stable) must be less than the solubility of carbon (metastable) at any given temperature." As I have pointed out, the critical temperature with which we are concerned in the phenomena of slow graphitization is the equilibrium temperature Ae_1 rather than the recalescent temperature

Ar_1. If the expression Ae_1 is substituted for Ar_1, the two statements in the sentence quoted are contradictory. That is, if the solubility of cementite at a given temperature exceeds that of graphite, the Ae_1 temperature of the iron-cementite system must be lower than that of the iron-graphite system instead of higher, as stated by Mr. Schwartz.

To the best of our knowledge, there is no difference between the austenite of a graphitized iron and the austenite of a white iron. In the first case the solid-solution phase is in equilibrium with particles of graphite, while in the second case the solid solution is in equilibrium with cementite. Since graphite is more stable than cementite, we assume that the austenite of white irons is richer in carbon at a given temperature than that of graphitized irons, in accordance with the general laws of chemical equilibria. In all other respects the austenites of the two systems are identical. In each case cooling at a moderate rate results in the formation of pearlite, while quenching produces martensite. Similarly, if the cold irons are dissolved in nitric acid the colored derivatives on which the color carbon test depends are the same. There is every reason to suppose that the atomic constitution of austenite is the same whether the excess phase is graphite or cementite.

The presence of carbon in solution in gamma iron lowers the temperature of its allotropic transformation. Granting that the constitution of austenite is always the same, the mechanism by which the transformation temperature is lowered is always the same and a given amount of carbon in solution will always produce the same lowering whether the excess phase is graphite or cementite. Hence the lowest temperature of transformation will occur in the system that permits the greatest concentration of carbon in solution in austenite, that is, the iron-cementite or metastable system. Ae_1 metastable must be lower than Ae_1 stable.

The same line of reasoning leads to the conclusion that if "the alloy reaches Ar_1 (Ae_1) very low in combined carbon, probably indefinitely near zero," then Ae_1 must be indefinitely near A_3 of a pure iron-silicon alloy containing the same amount of silicon but no carbon; Ae_1 (stable) would then be nearer 900° C. than 680° C. This we know is not the case. The temperature of Ae_1, as shown by reheating experiments on annealed irons, for a silicon content of about 0.85 per cent., lies between 740° and 775° C. This range of temperature also includes the Ae_1 point of the corresponding cementite system. This indicates that the eutectoid composition is likewise nearly the same in the two systems.

Mr. Schwartz has referred to Mr. Bean's values of 727° C. for Ar_1 of an annealed iron and of 746° C. for a corresponding white iron and takes this as evidence that the critical point of the stable system is below that of the metastable. My interpretation of these figures is somewhat different. In the first place, the phase change recorded as Ar_1 in the cooling curves is identical in the two irons. If an annealed malleable iron is

heated above the critical temperature, part of the graphite goes back into solution; then on cooling at a rate suitable for taking a cooling curve, most of the carbon of this solid solution is precipitated in the form of pearlite. The Ar_1 of the cooling curve is, therefore, the temperature of the pearlite transformation on cooling, whether the specimen is malleable iron or white iron. The fact that Ar_1 occurs at a higher temperature in the white iron is due simply to the presence of an abundance of structurally free cementite nuclei, which are practically absent in the annealed iron. Doctor Howe has shown that the Ar_1 point of a eutectoid steel can be depressed by increasing the maximum temperature to which the steel is heated, because of the more thorough destruction of cementite nuclei. This effect is accentuated in the present case because of the great amount of free cementite in the white iron.

The curve Mr. Schwartz plotted from my data contains a slight error. The combined carbon content for 785° C. (set *E*) was shown to be between 0.66 and 0.85 per cent.; the definite value of about 0.68 per cent. plotted by Mr. Schwartz is, therefore, uncertain. I believe that this point should lie farther to the right.

Mr. Schwartz' observation that the values obtained for combined carbon are not the same on reheating a graphitized metal as on annealing a white iron to equilibrium is very odd. The single experiment I made on this point gave identical results by the two methods. It is generally understood that a system is not in a state of equilibrium unless the same condition is reached by approaching from either side. If the observation noted by Mr. Schwartz can be experimentally verified, we must suspect that we are not dealing with true equilibrium.

Malleableizing of White Cast Iron*

By Arthur Phillips, M. S.,† New Haven, Conn., and E. S. Davenport, M. S.,‡ Naugatuck, Conn.

(New York Meeting, February, 1922)

The purpose of this paper is to present certain data and observations resulting from a series of experiments dealing with the heat treatment and microstructure of commercial white cast iron and its derivative, malleable iron. In planning the experimental work, particular pains were taken to secure for the tests white cast iron of "normal" composition; *i.e.*, within the composition limits commonly prescribed by manufacturers of malleable castings. A review of the literature leads us to believe that much data of a fragmentary character treating of the graphitization of white cast iron have been of little value, mainly because of the diversity in chemical composition of the materials employed in the tests. Moreover, when feasible, annealing periods at least comparable to those of current practice have been adopted.

We wish to acknowledge our indebtedness to the members of the research department of the Eastern Malleable Iron Co. for the white cast iron used in the tests and, particularly, for their active coöperation during the experimental stage of the work.

In this paper the following subjects will be discussed in the order indicated: Data on the thermal critical points of white cast iron and malleable iron. Changes produced in tensile properties and microstructure of white cast iron by annealing at different temperatures within the range, 760 to 1100° C. Relation of thickness of wall section of hard iron to microstructure and tensile properties of malleable iron obtained under normal annealing conditions. Notes on mechanics of graphitization of normal white cast iron as observed in specimens quenched after various periods of anneal at approximately 800° C.

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Data on the Thermal Critical Points of White Cast Iron and Malleable Iron

The American "malleableizing" process consists essentially of a lengthy heat treatment at a moderately high temperature, followed by extremely slow cooling, with the object of converting the cementite of the white cast iron into graphite, or "temper" carbon, and ferrite. From the physicochemical point of view, the changes involved during this treatment are extremely complicated and are not thoroughly understood at the present time. Typical white iron structures are shown in Figs. 1 and 2; Fig. 3 is representative of normal "black heart" malleable casting.

The exact temperature at which temper carbon begins to form has been greatly disputed. Some investigators believe that the change is initiated at, or slightly above, the A_1 point; others hold that graphitization can take place below the lower critical temperature. This point will be discussed elsewhere in this paper and some experimental results bearing on the subject will be offered.

As it is generally assumed that the temperature of initial precipitation of temper carbon is approximately the lower critical temperature of the material in question, it seems desirable to have precise information regarding the Ac_1 and Ar_1 points of normal hard iron. The literature records the results of a number of investigators who have determined the critical temperatures of cast iron covering a wide range of composition;

Table 1.—*Critical Temperatures of Cast Iron*

Ar_1 Point, Degrees C.	Ac_1 Point, Degrees C.	Carbon Content, Per Cent.	Silicon Content, Per Cent.	Observers
740–750		3.96	1.14	Wust and Peterson[a]
726		2.95	0.68	Hague and Turner[b]
730		2.56	0.97	Hague and Turner[b]
734		2.70	1.19	Hague and Turner[b]
700	715	2.00	1.1	Charpy and Cornu-Thenard[c]
693	732	Not given	Not given	Schwartz[d]
746	763	2.58	0.87	Bean[e]
745	765	2.40	0.90	Hammond Laboratory

[a] Wust and Peterson: Beitrag zum Einfluss des Siliciums auf das System Eisen-Kohlenstoff. *Metallurgie* (1906) **3.**

[b] Hague and Turner: Influence of Silicon on Pure Cast Iron. *Jnl.* Iron and Steel Inst. (1910) **82.**

[c] Charpy and Cornu-Thenard: Researches on Iron, Silicon and Carbon Alloys. *Jnl.* Iron and Steel Inst. (1915) **91.**

[d] H. A. Schwartz: Some Physical Constants of American Malleable Cast Iron. *Proc.* Amer. Soc. Test. Mat. (1919) **19,** Pt. 2, 247.

[e] W. R. Bean: Discussion of Schwartz' paper.

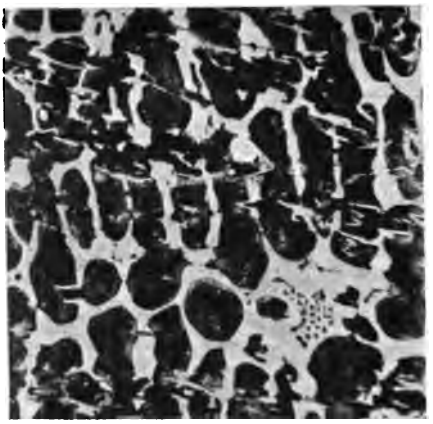

FIG. 1.—NORMAL WHITE CAST IRON. × 250.

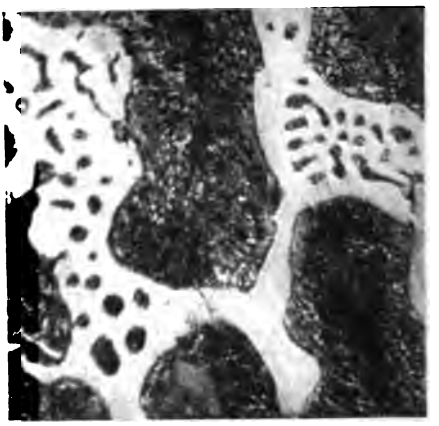

FIG. 2.—LEDEBURITE IN WHITE CAST IRON. ×750.

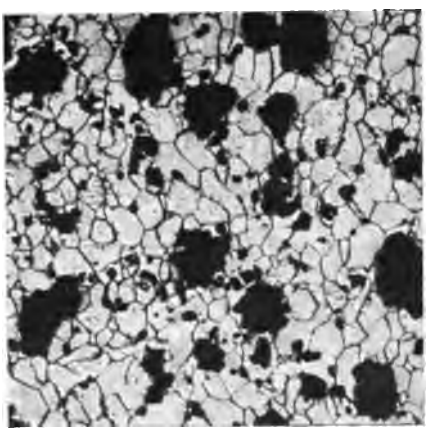

FIG. 3.—NORMAL MALLEABLE CAST IRON. × 100.

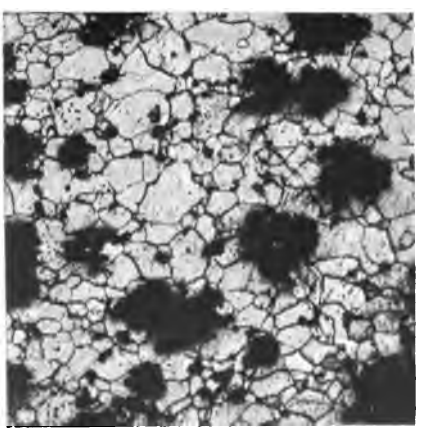

FIG. 4.—ANNEAL I. HOTTEST POT IN MILL FURNACE. × 100.

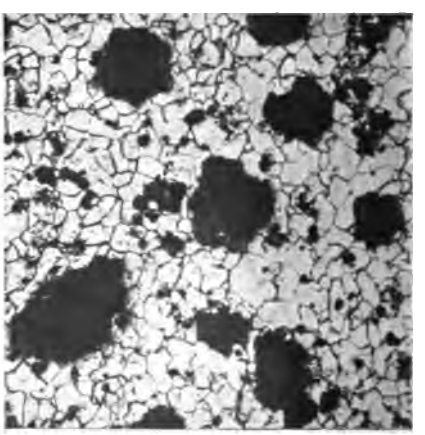

FIG. 5.—ANNEAL II. COOLEST POT IN MILL FURNACE. × 100.

SPECIMENS WERE ETCHED WITH 5 PER CENT. NITRIC ACID IN ALCOHOL.

Table I summarizes what seem to be the most significant and valuable data available.

The results of Schwartz and Bean are of especial interest as they were obtained, presumably by Schwartz and without doubt by Bean, on material of normal composition from the viewpoint of the manufacture of malleable castings. Schwartz' results, admittedly, were lacking in precision, and are, undoubtedly, low; Bean's values are fairly consistent with the results of earlier investigators, particularly Hague and Turner.

In order to obtain additional data, the writers made careful determinations on white cast iron and commercial malleable iron; the malleableized specimens showed no combined carbon and apparently had been properly and thoroughly annealed. The specimens were of the following compositions:

	Sulfur, Per Cent.	Manganese, Per Cent.	Phosphorus, Per Cent.	Silicon, Per Cent.	Total Carbon, Per Cent.
White cast iron.....	0.083	0.30	0.160	0.90	2.40
Malleable iron.....	0.108	0.28	0.193	0.81	2.35

The specimens were taken from the central portions of standard A. S. T. M. tensile bars, and had holes into which the hot junction of a

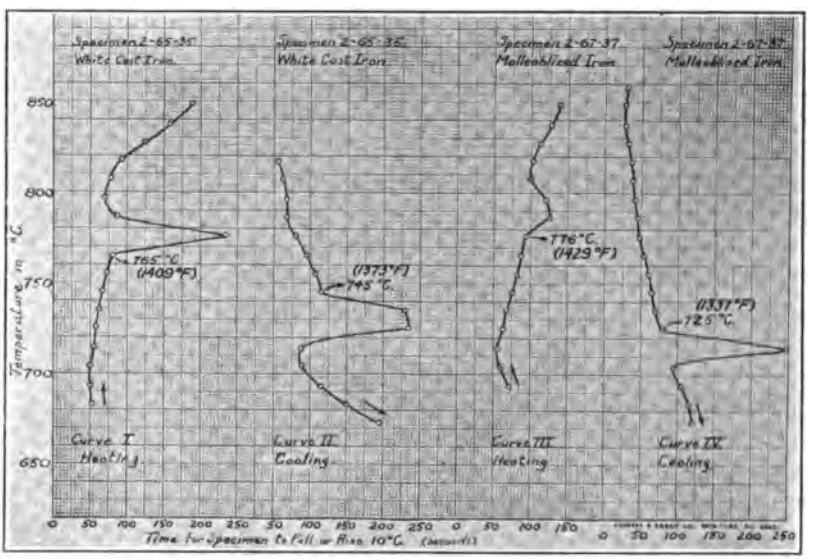

Fig. 6.—Critical-point curves.

Pt-PtRh thermocouple, in series with a high-resistance galvanometer, was inserted. An electric-resistance muffle furnace was used in these and in all laboratory annealing treatments described here. Inverse-rate heating and cooling curves are shown in Fig. 6, and the critical points Ac_1 and Ar_1 taken as the temperatures corresponding to the beginning

of the break in each curve, reading from bottom to top in the case of heating and from top to bottom in the case of cooling.

There is some difference of opinion as to the proper interpretation of critical-point data from inverse-rate curves. Some writers believe that the peak of the break should be taken as the true value for the point, others argue that the beginning of the break should be taken. We are inclined to agree with Howe that the first inflection in the curve, that is the beginning of the transformation, should be regarded as the significant temperature. This interpretation enables us to compare our results directly with those of Bean, which with the curves in Fig. 6 show that our results agree closely. In our opinion 745° C. may be regarded as the Ar_1 point for hard irons cooled at the rate of approximately 1° C. per second.

As, however, the rate of cooling (4° to 5° C. per hr.) found imperative in malleableizing practice is extremely slow and the temperature of anneal (approximately 780° C.) does not greatly exceed the Ar_1 point determined under ordinary conditions, it is conceivable that the real and significant critical point is more nearly Howe's Ae_1 temperature, that is, some temperature between the Ar_1 and Ac_1 points as indicated by the conventional cooling-curve determinations. It is interesting to note that Archer[1] believes that "for a 1.0-per cent. silicon iron, the A_1 point is probably within 15° of 750° C."

It is to be noted that, in both sets of results, the gap between Ac_1 and Ar_1 is much greater in the case of the malleableized specimens than in the case of the white cast iron. An examination of the curves (Fig. 6) shows that the thermal effect, as shown on the heating curve of the malleableized specimen, is very small. This can be explained on the basis of the theory that it is only the combined carbon which takes part in the transformation at A_1. In the malleableized specimens, the combined carbon content was extremely low, in fact, so low that no cementite could be detected under the microscope at ordinary magnifications. The relatively large amount of temper carbon, while having little effect on the Ac_1 transformation, did have a decided effect on the Ar_1 point of the same iron. At some temperature near the Ac_1 point (probably at Ac_1 exactly), the iron began to dissolve some of the temper carbon, absorbing more and more as the temperature was raised. Upon cooling at a relatively rapid rate, this dissolved carbon did not have time to precipitate again as temper carbon, but came out of the solution as combined carbon in the form of pearlite, with possibly a small amount of pro-eutectoid cementite. Thus, we would expect a greater thermal effect on the cooling curve than on the heating curve, which is the case. The re-solution of

[1] R. S. Archer: Graphitization of White Cast Iron. See page 446.

free carbon upon heating graphitic irons above A_1 has been conclusively shown by other investigators, notably Touceda[2] and Archer.[3]

Changes Produced in Mechanical Properties and Microstructure of White Cast Iron by Annealing at Different Temperatures Within the Range 760–1100° C.

This series of experiments was begun primarily to determine the effect of variation in temperature, of the order commonly found in commercial annealing furnaces, on the structure and tensile properties of the completely malleableized product.

It has long been known that extremely high temperatures will cause so-called burned castings, the characteristics of which are: excessive decarburization, intercrystalline oxidation near the surface of the casting, a reduction in strength and ductility and a general deterioration of the product. Fortunately, these extremely high-temperature anneals are rare. In the commercial furnace of average dimensions, however, there is always a pronounced thermal gradient, so that castings nearest the firebox reach a much higher temperature and have a longer annealing period than those at the opposite end of the furnace. For this reason, they might show quite different tensile properties and microstructure.

Occasionally, castings of normal chemical composition and apparently normal heat treatment yield poor tensile properties; the microstructures appear to be normal in most cases, except possibly for a somewhat coarser ferrite and temper-carbon structure. It has long been a question as to whether the coarser structures could be associated with the poor physical properties of these castings and whether such structures had been caused by a high-temperature anneal; that is, a temperature not high enough to "burn" the castings but high enough to modify the mechanical properties. White and Archer[4] have shown that high-temperature anneals tend to coarsen the temper-carbon nodules and cause a deterioration in mechanical properties. They did not, however, show how the ferrite matrix, which is the main body of the casting, was affected by the higher temperature, nor did they offer data correlating deterioration in tensile properties with high-temperature anneals. It has always been assumed that the coarse structures of malleable iron are due to high annealing temperatures. Except the work mentioned, so far as we are aware, no investigations on the subject have been reported.

In order to determine the magnitude of the thermal gradient in a commercial annealing furnace and, more particularly, to furnish data

[2] E. Touceda: Research on Malleable Iron. *Trans.* Am. Soc. Mech. Eng. (1919) **41.**

[3] *Loc. cit.*

[4] A. E. White and R. S. Archer: Annealing of Malleable Castings. *Trans* Amer. Foundrymen's Assn. (1918) **27.**

associating differences in microstructure and tensile properties with such temperature variation, the following heat treatments were carried on. The material used consisted of a set of thirty standard A. S. T. M. tensile-test bars cast from a regular mill heat; the fracture of the material as cast was clear white and perfectly normal in all respects. Its composition was: silicon 0.90 per cent., manganese 0.30 per cent., sulfur 0.083 per cent., phosphorus 0.160 per cent., total carbon 2.40 per cent.

Bars Annealed in a Mill Furnace

Anneal I.—Four bars were packed in the hottest pot of a commercial annealing furnace of average dimensions [11 by 16 by 8 ft. high to spring of arch, firebox in corner, 9 sq. ft. (0.8 sq. m.) of grate area]; briefly stated, they were annealed "top pot, firebox." An iron-constantan thermocouple was placed in the furnace in such a way that the end of the protecting tube was in direct contact with the pot containing the bars.

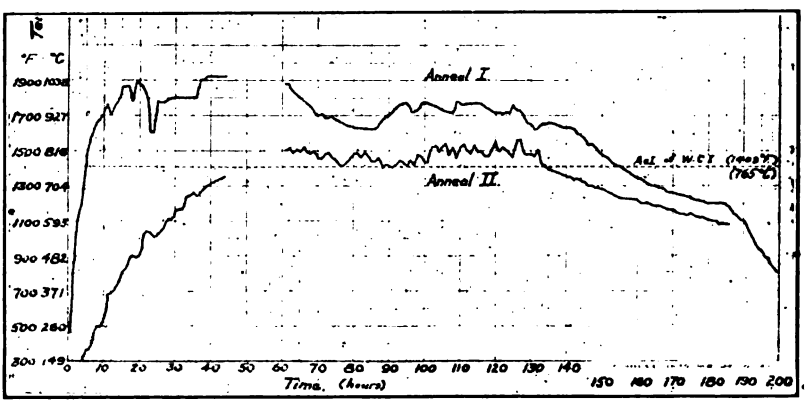

FIG. 7.—TEMPERATURE RECORD OF MILL ANNEAL.

Anneal II.—Four bars were packed in a similar manner in one of the coolest pots in the same furnace; that is, they were annealed in a pot at the opposite end of the furnace, or in the "bottom pot, front middle." A thermocouple was also placed in this end of the furnace, the hot junction end of its casing being in direct contact with the pot containing the bars; both thermocouples were connected to a Leeds & Northrup automatic temperature recorder. The furnace was charged as usual, fired for five days, and then allowed to cool at the rate of about 4° C. per hr.; in other words, the material was given a perfectly normal anneal. Curves I and II, Fig. 7, are the temperature records of the hottest and coolest pots, respectively. The break in each curve was caused by the recorder mechanism's getting out of adjustment one night. There is good reason for believing, however, that at no time during this interval did the temperature get above the maximum temperature recorded by the instrument. It is to be noted that, after the furnace had reached the

annealing temperature, there was a difference of about 140° C. between the hottest and coolest sections; also, that the bars of Anneal I were above the critical range for about 150 hr. while the bars of Anneal II were above it for approximately 85 hours.

The results of the tensile tests are summarized in Table 2. It is evident that a thermal gradient of the order encountered in this anneal, which may be regarded as representative of current practice, has little or no significance if the ordinary tensile test is regarded as a criterion of quality. All tests successfully met the A. S. T. M. specifications.[5] Fig. 4 shows the structure of the material annealed at the higher temperature and Fig. 5 the structure of the iron annealed at the lower. Although there is apparently little or no difference in the size of the temper-carbon areas produced, there seems to be a difference in the physical condition of the graphitic masses; the graphite in Fig. 5 is more compact and more sharply outlined than in Fig. 4. The higher temperature has apparently produced a somewhat coarser ferrite matrix.

The differences in both the tensile properties and the microstructures of the two sets are so slight, however, that we seem justified in concluding that, in spite of the marked temperature gradient and the considerable difference in time above Ac_1, castings annealed in a commercial furnace under such conditions will be of reasonably high quality.

TABLE 2.—*Tensile Properties of Bars Annealed in Hottest and Coolest Pots of a Commercial Annealing Furnace*

Anneal Number	Bar Number	Diameter, Inch	Yield Point, Lb. per Square Inch	Ultimate Strength, Lb. per Square Inch	Elongation in 2 In., Per Cent.	Remarks
I	1	0.637	36,242	52,747	14.0	Annealed in hottest pot
I	2	0.639	35,609	52,229	14.0	
I	3	0.636	35,616	54,865	16.5	
I	4	0.649	35,821	52,431	14.0	
Average			35,822	53,063	14.6	
II	1	0.643	38,771	53,738	18.5	Annealed in coolest pot
II	2	0.640	39,602	51,911	11.5	
II	3	0.634	38,248	55,020	15.5	
II	4	0.637	37,495	54,457	12.5	
Average			38,529	53,782	14.5	

Bars Annealed in Laboratory

In order to determine the effect of annealing temperatures covering a range not usually encountered in a commercial furnace, several lots of bars were annealed in the laboratory.

[5] Specifications: Tensile strength 45,000 lb. per sq. in. (3163.9 kg. per sq. cm.); elongation in 2 in. (5 cm.) 7½ per cent.

Anneal III, High Temperature (1100° C.).—Two bars were packed in sand in a cast-iron tube, capped at both ends, 23 in. (58 cm.) long and 2½ in. (6.4 cm.) in diameter. A Pt-PtRh thermocouple, enclosed in a thin iron casting, was inserted through one end of the tube in such a manner that the hot junction was between the bars and at a point midway between their ends, as shown in Fig. 8. The tube was placed in an electric-resistance muffle furnace of suitable dimensions consisting essentially of an alundum-tube wound with nichrome wire, surrounded by pea-size firebrick held in an asbestos board container. The tube ends and furnace openings were sealed as effectively as possible and the bars annealed for 55 hr. at the highest temperature attainable, approximately 1100° C. (actually 1090° ± 10°). At the end of this time, the bars were cooled in the furnace at a rate approximating 10° C. per hr. until

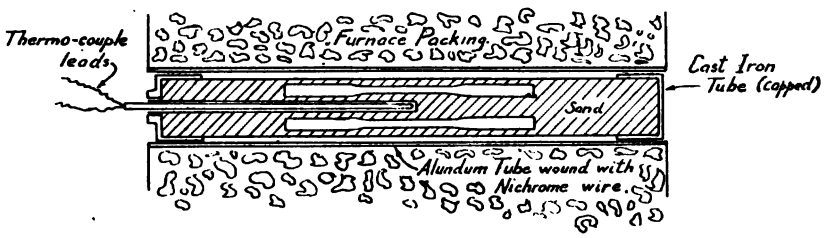

FIG. 8.

800° had been reached; the specimens were then cooled at the rate of about 5° per hour until well below the critical range. A Leeds & Northrup recorder furnished a complete record of temperature variation. The thermocouple and recorder were carefully standardized by running freezing-point determinations on pure metals before and after each anneal described.

After being broken in tension, the bars showed a partial white fracture. It later developed that this was due to too rapid cooling through the critical range. The tension test values were, of course, affected by the pearlite causing this partial white fracture, and for this reason, the tests were repeated, as described under Anneal IV.

Anneals IV to IX.—All of the anneals of this series were conducted under the conditions described in detail under Anneal III. A summary of the annealing data is to be found in Table 3.

All of the bars annealed in the laboratory were machined to 0.505 in. (12.8 mm.) diameter before breaking. The purpose of this machining was twofold: (1) To eliminate any effects of the decarburized layer which would vary in depth with the temperature of anneal; that is, to obtain tensile data representative of the "heart" or real body of the casting. (2) To facilitate the measurement of percentage reduction in area. The machining of the bars may be open to criticism, since it is contrary to

TABLE 3.—*Summary of Annealing Data*

Anneal Number	Temperature of Anneal, Degrees C.	Period of Anneal, Hours	Rate of Cooling, Degrees C. per Hour	Fracture[a]	Remarks
III	1100	55	10 to 800 5 to 650	Approximate, 40 per cent. white	White fracture due to too rapid cooling.
IV	1100	60	10 to 770 4 to 650	Normal black	
V	785	63	4 to 650	Approximate, 10 per cent. white	
VI	830	70	3 to 700	Normal black	
VII	770	93	2½ to 650	White	Temperature never below Ac_1
VIII	770	121	4 to 650	White	
IX	750	98	4 to 650	White	

[a] With the exception of Anneal III, all of the white fractures recorded were due to insufficient time at the temperature specified and not to too rapid cooling.

practice, but this seemed to be the most feasible way of eliminating an objectionable variable, namely, decarburization. A set of bars annealed at the temperature ordinarily obtained in commercial work (788° C.), and then machined before breaking, furnished a reference point for the tensile properties of machined bars.

The tensile test results obtained on these bars are recorded in Table 4.

TABLE 4.—*Tensile Properties of Bars Annealed in the Laboratory*

Bar	Number	Diameter, Inch	Yield Point, Lb. per Square Inch[a]	Ultimate Strength, Lb. per Square Inch	Elongation in 2 In., Per Cent.	Reduction in Area, Per Cent.
III	1	0.505	41,350	57,550	15.0	11.6
III	2	0.503	36,390	56,170	17.0	12.7
IV	1	0.507	32,630	45,450	15.5	13.3
IV	2	0.504	32,760	45,880	14.5	11.0
V	1	0.503	36,880	48,240	9.0	10.5
V	2	0.505	35,500	50,250	12.5	10.0
VI	1	0.505	32,400	48,700	14.0	13.0
VI	2	0.505	33,000	46,800	10.0	11.0
VI	3	0.506	36,800	47,800	9.5	10.2
VII	1	0.505	39,600	53,250	5.5	3.5
VII	2	0.505	40,600	56,250	6.0	3.0
VIII	1	0.504	40,000	56,880	5.0	1.5
VIII	2	0.502	43,700	61,310	4.0	2.5
IX	1	0.506	51,140	63,420	2.0	1.5
IX	2	0.505		62,800	2.0	1.0

[a] As obtained by the "beam-drop" method.

It will be noted (Table 3) that normal black fractures were obtained after two anneals only, namely, at 1100° and 830° C. From the standpoint of tensile strength, the lower temperature (830°) anneal yields values slightly higher than the 1100° C. anneal; from the standpoint of ductility, however, the higher temperature anneal gives somewhat higher

values. The higher tensile-strength and yield-point values and the lower ductility values of the other anneals must be attributed to the presence of combined carbon, and not to any specific properties of the ferrite matrix or temper carbon areas.

As stated before, the annealing of white iron seems to permit of considerable latitude (with respect to temperature) without causing serious deterioration as measured by the tensile test. We believe, with Rawdon,[6] however, that the tensile test does not sharply or adequately differentiate between two metals of the same chemical composition that differ only in the degree of fineness of the structural elements. It is quite probable that shock or impact tests on this material would have indicated more faithfully the significance of variation in the grain size of the ferrite matrix and the temper carbon areas.

Microstructures of Annealed Bars

Anneal III, (1100° C.).—Fig. 9 is the microstructure of the portion of the bar showing black fracture; Fig. 10 is representative of the portion showing white fracture. It is evident that the partial white fractures were caused by too rapid cooling through the critical range, since the so-called "bull's eye" structure of Fig. 10 is always associated with rapid cooling at that stage.

Anneal IV, (1100° C.).—Figs. 11 and 12 are representative of the microstructure of each bar; no combined carbon was noted in either specimen. The coarse irregular temper-carbon particles and the coarse-grained ferrite of the matrix, also the suggestion of radial growth of the ferrite about the temper-carbon spots, bear out the results of Anneal III. The coarseness of these structures is brought out more forcibly by a comparison with the structure of Fig. 5. It is obvious that a high annealing temperature (1100° C. or over) results in a coarse irregular type of temper carbon, and a coarse-grained ferrite matrix.

Anneal V, (785° C.).—Fig. 13 is representative of the microstructure of these bars and shows that a certain amount of combined carbon was present after annealing. The structure produced, however, is much finer than that shown in Figs. 9, 11, and 12, and, except for the cementite, is more like that shown in Fig. 5.

Anneal VI, (830° C.).—Fig. 14 is thoroughly representative of the microstructure of white iron annealed at 830° C. It is to be noted that, although the temper-carbon spots are rather coarse, the ferrite grain is much finer than in the bars annealed at the higher temperatures.

Anneal VII, (770° C.).—Fig. 15 shows the presence of cementite; Fig. 16, the same specimen etched with sodium picrate, reveals the cemen-

[6] H. S. Rawdon: Effect of Metallic Structure Upon Properties. *Chem & Met Eng.* (1921) **24**, 523.

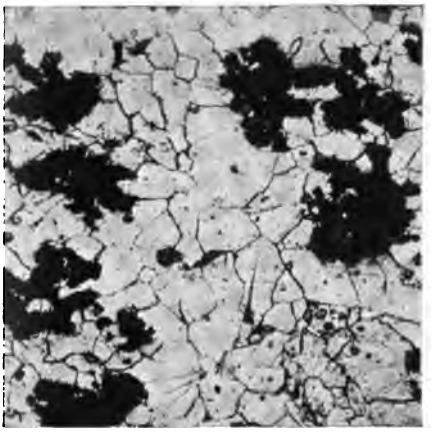

FIG. 9.—ANNEAL III. 55 HR. AT 1100° C. × 100.

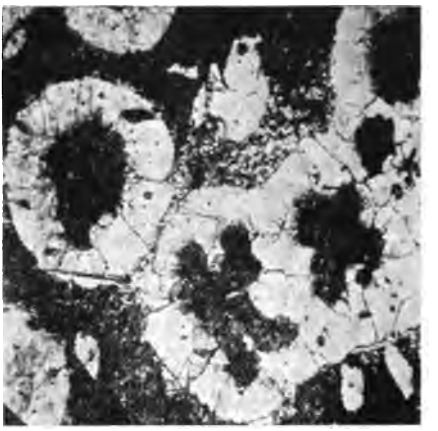

FIG. 10.—ANNEAL III. 55 HR. AT 1100° C. × 100.

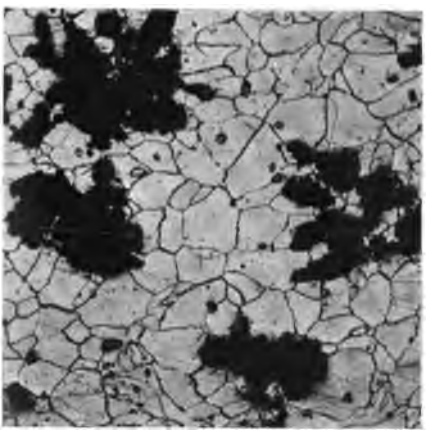

FIG. 11.—ANNEAL IV. 60 HR. AT 1100° C. × 100.

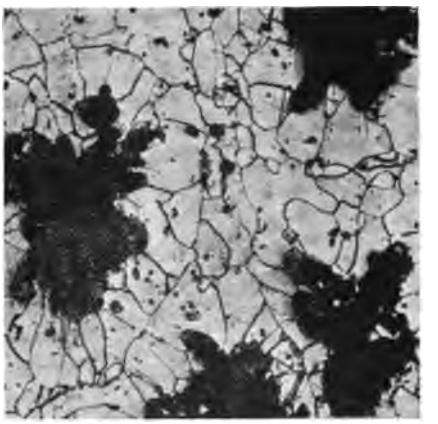

FIG. 12.—ANNEAL IV. 60 HR. AT 1100° C. × 100.

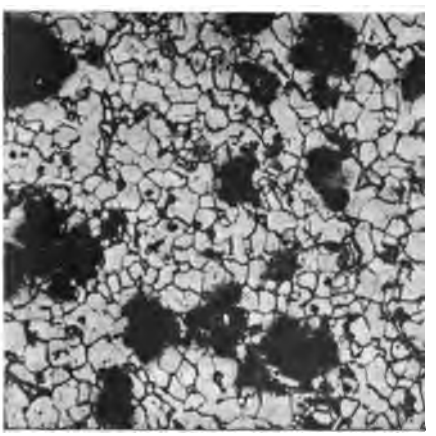

FIG. 13.—ANNEAL V. 63 HR. AT 785° C. × 100.

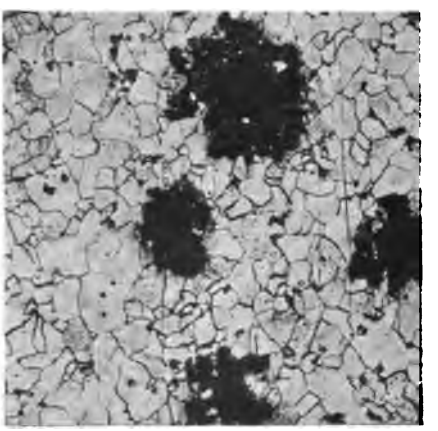

FIG. 14.—ANNEAL VI. 70 HR. AT 830° C. × 100.

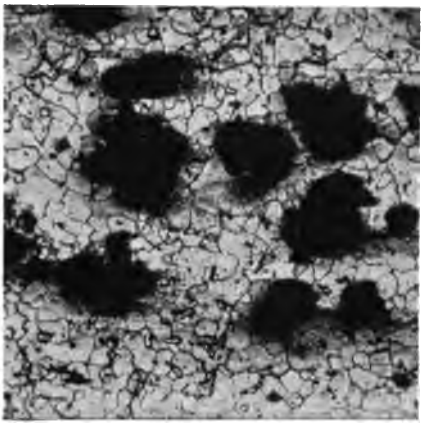

FIG. 15.—ANNEAL VII. 93 HR. AT 770° C. × 100.

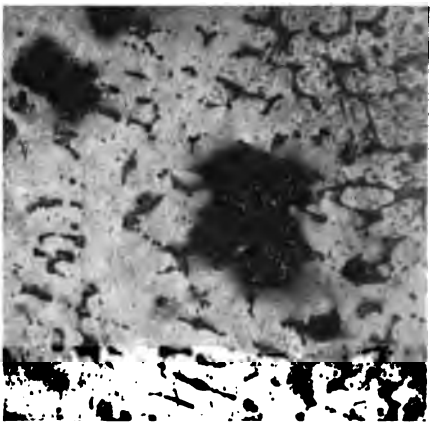

FIG. 16.—SAME AS FIG. 15, ETCHED WITH SODIUM PICRATE. × 100.

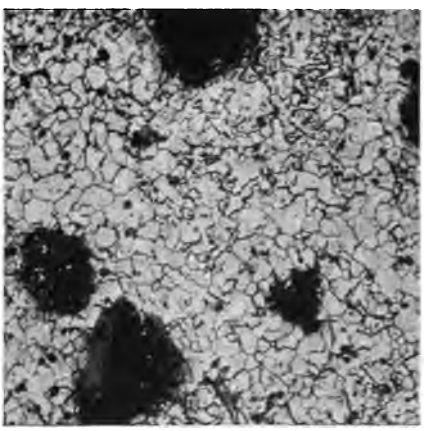

FIG. 17.—ANNEAL VIII. 121 HR. AT 770° C. × 100.

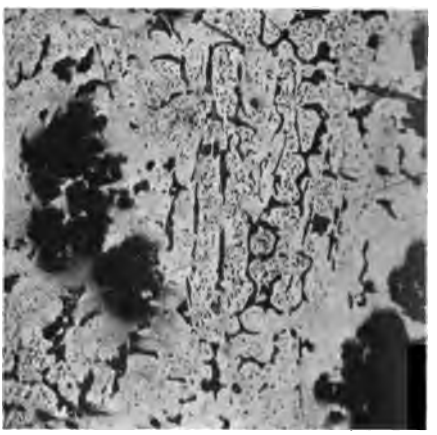

FIG. 18.—SAME AS FIG. 17, ETCHED WITH SODIUM PICRATE. × 100.

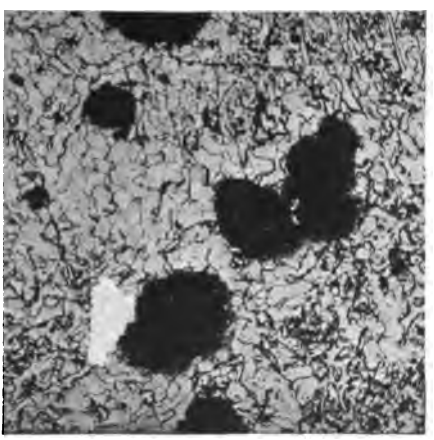

FIG. 19.—ANNEAL IX. 98 HR. AT 750° C. × 100.

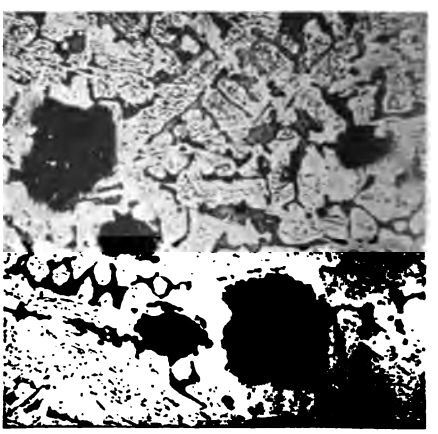

FIG. 20.—SAME AS FIG. 19, ETCHED WITH SODIUM PICRATE. × 100.

tite more clearly. The ferrite is not much finer in grain than that shown in Fig. 13 but the temper-carbon particles are somewhat larger, more regular in outline, and more compact. The cementite, in Figs. 13, 15, and 16, is of the massive variety, and is caused by insufficient temperature during anneal, rather than of the pearlitic or sorbitic variety, which is caused by too rapid cooling, as in Fig. 10. An examination of structures and tensile data of anneals III, V, and VII leads to the conclusion that pearlitic or sorbitic cementite from rapid cooling, even though there is more of it, is much less harmful from the standpoint of ductility than the massive cementite resulting from under-annealing.

Anneal VIII, (770° C.).—This heat treatment was the second attempt to get complete graphitization at this temperature (just above Ac_1) by using a longer annealing period. Figs. 17 and 18 show that the attempt was unsuccessful, as there was almost as much massive cementite in these specimens as in Figs. 15 and 16. Attention is called to the fine-grained ferrite and the rather large, regularly outlined temper-carbon particles of Fig. 17.

Anneal IX, (750° C.).—These bars, annealed at a temperature just below the Ac_1 of white cast iron, were entirely white in fracture. Figs. 19 and 20 show the large amount of massive cementite remaining in the bars after annealing. Attention is called to the fine-grained ferrite and the compact, regularly outlined temper-carbon particles. It might take from two to three weeks to graphitize completely at this temperature.

The study of the microstructure of the bars described leads to the following conclusions:

1. The ferrite grain size increases with the temperature and, probably, with the time of anneal.

2. The temper-carbon areas produced at the lower temperatures are more compact and sharply outlined than the graphitic areas obtained at the higher temperatures. High-temperature temper carbon is, in general, characterized by a more or less porous structure of ragged and "spidery" outline. The higher temperatures have a disintegrating effect on the compact and rounded masses characteristic of carbon precipitated at the lower temperatures.

Relation of Thickness of Wall Section of White Cast Iron and the Microstructure and Tensile Properties of Malleable Iron Obtained under Normal Annealing Conditions

The relation between the thickness of the casting section of white cast iron and the microstructure and mechanical properties of the malleable iron obtained from the hard iron, should be of considerable interest to those engaged in the production of malleable castings. Presenting the problem a little differently, the manufacturer is interested in the effect of the rate of cooling of the hard casting on the mechanical

FIG. 21.—WHITE CAST IRON. × 100.

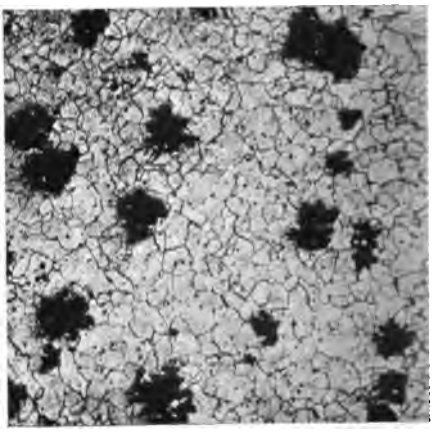

FIG. 22.—SAME AS FIG. 21, ANNEALED. × 100.

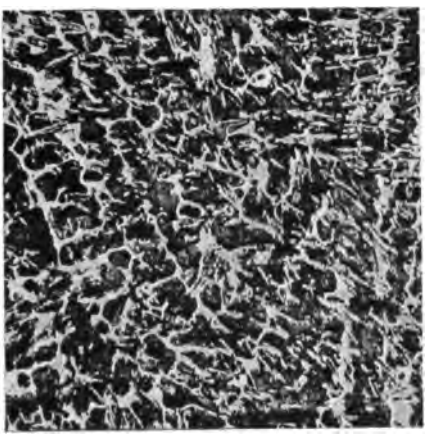

FIG. 23.—WHITE CAST IRON. × 100.

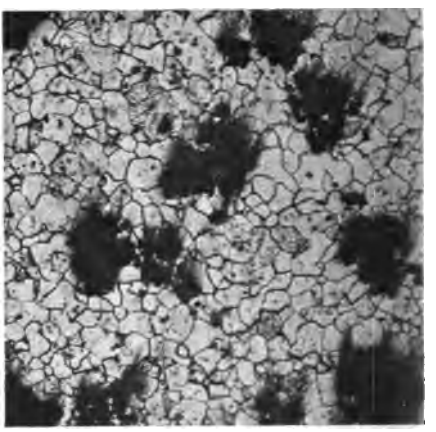

FIG. 24.—SAME AS FIG. 23, ANNEALED. × 100.

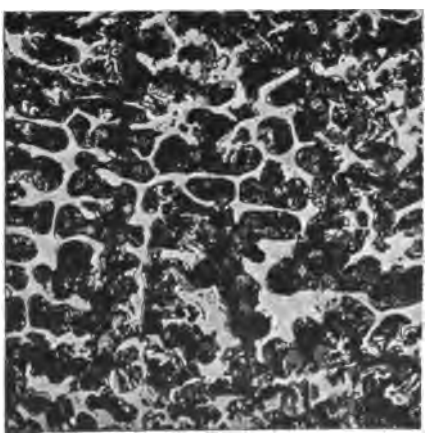

FIG. 25.—WHITE CAST IRON. × 100.

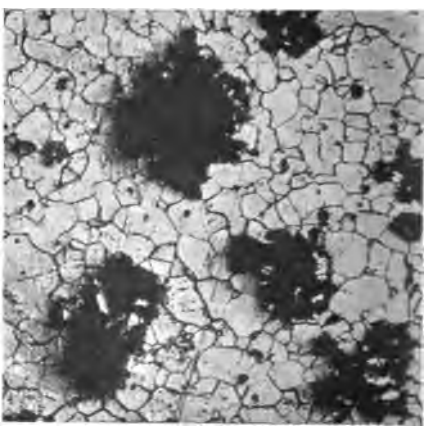

FIG. 26.—SAME AS FIG. 25, ANNEALED. × 100.

SPECIMENS WERE ETCHED WITH 5 PER CENT. NITRIC ACID IN ALCOHOL

properties of the malleable casting subsequently obtained (assuming constant chemical composition).

In a recent paper,[7] micrographs of three specimens of different thickness annealed at a common temperature seemed to indicate that the size of the ferrite and temper-carbon areas increased with the wall thickness. As far as we are aware, no direct comparison between the structural characteristics of malleable iron and the original white-iron castings of varying thickness have been published.

To add to our knowledge on this subject, we secured a white-iron casting, in the form of a wedge, of the same composition as was used in the other experiments. Figs. 21, 23, and 25 show the structure of three cross sections corresponding to the following dimensions. The section shown in Fig. 21 was 1 by 0.05 in. (25.4 by 0.127 mm.); that shown in Fig. 23 was 1 by 0.25 in. (25.4 by 0.64 mm.); and that shown in Fig. 25 was 1 by 0.45 in. (25.4 by 1.14 mm.).

As might be expected, the rapid cooling in the lightest section (Fig. 21) has produced a finely divided mixture of pearlite and cementite and the structural elements become coarser as the wall thickness increases, *i.e.*, as the rate of cooling decreases.

The three specimens were then packed in sand and annealed with the bars of Anneal VI (Table 3); the resulting structures are shown in Figs. 22, 24, and 26.

A comparison of the hard-iron structures and the corresponding malleable structures indicates that: (1) the finer the hard-iron structures the finer will be the ferrite grain and temper-carbon areas of the malleable iron; (2) the effect of the wall thickness, and therefore the rate of cooling of the white cast iron, is more pronounced in the case of the temper-carbon areas than in the case of the ferrite.

Although no tensile data was obtained in this experiment, direct comparison of the structures described with those corresponding to known tensile properties leads to the conclusion that variations in wall section cause more pronounced variations in mechanical properties than can be attributed to the thermal gradient incidental to ordinary mill anneal. Doubtless poor mechanical properties are often obtained due to the additive effect of a very high annealing temperature and a heavy wall section.

Notes on Mechanics of Graphitization of Normal White Cast Iron as Observed in Specimens Quenched at Approximately 800° C.

Briefly stated, the completely cooled normal white iron consists of pearlite and cementite. There are, however, four kinds (from the view-

[7] Bean, Highriter and Davenport: Fractures and Microstructures of American Malleable Cast Iron. *Trans.* Amer. Foundrymen's Assn. (1920) **29.**

point of origin and state of aggregation) of cementite, namely: massive pro-eutectic cementite, eutectic cementite, pro-eutectoid cementite, eutectoid cementite (pearlite).

In some instances, it is possible to distinguish all of these elements within a rather limited area; more often, however, we are unable to make these deductions with any degree of assurance. The massive pro-eutectic cementite results from supercooling as indicated by the prolongation of line AB in Fig. 27.

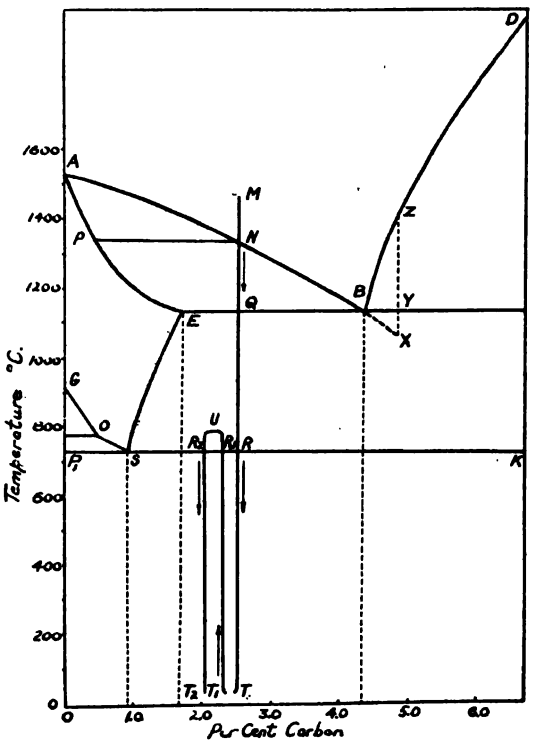

FIG. 27.—IRON-CARBON EQUILIBRIUM DIAGRAM.

Fig. 1 is typical of the structure of rapidly cooled cast iron. The ledeburite (eutectic) in the lower right-hand corner is small in amount because of the large amounts of structurally free cementite resulting from supercooling; the pro-eutectoid cementite is in the form of needlelike areas. The dark areas consist of pearlite formed by the transformation of the austenite at the A_1 point.

Much has been written on the general subject of the graphitization of gray and malleable iron. The earlier investigators in this field apparently believed that it is essentially the structurally free and metastable cementite that decomposes at the higher temperatures to form

ferrite and graphite, or temper carbon. More recently, however, several investigators, notably Storey,[8] Archer,[9] and Merica[10] have suggested the possibility of graphitization direct from solid solution. The writers have been of this opinion for some time and submit micrographs that, although not necessarily conclusive on this point, tend to indicate that, under ordinary treatment of white cast iron, temper carbon is formed directly from the solid-solution areas and not, in general, from the massive cementite areas.

Specimens of white cast iron of normal composition (*i.e.*, same composition as used in critical point annealing experiments) were packed in sand in small fireclay containers. The containers were then placed in an electric-resistance muffle furnace and heated to 800°C. At predetermined intervals, arbitrarily chosen, one specimen was drawn from the furnace and quenched by throwing the container into a large body of cold water. The containers were opened as soon as they struck the water and the specimens subjected to the quenching action. The marking and treatment of the specimens are summarized in Table 5.

TABLE 5

Specimen No.	Treatment	Specimen No.	Treatment
G0	Quenched after reaching 800° C.	G5	Quenched after 18 hr. at 800° C.
G1	Quenched after 3 hr. at 800° C.	G6	Quenched after 25 hr. at 800° C.
G2	Quenched after 8 hr. at 800° C.	G7	Quenched after 48 hr. at 800° C.
G3	Quenched after 12 hr. at 800° C.	G8	Quenched after 60 hr. at 800° C.
G4	Quenched after 15 hr. at 800° C.		

Discussion of Microstructure Obtained

Figs. 28 to 36 show the microstructures representative of each specimen in the series at 100 diameters; Figs. 37 to 45 show the same specimens at higher magnifications. It is evident that during the earlier stages of anneal, the only visible changes taking place are the coarsening of the pearlite lamellæ and perhaps a slight spheroidizing of the proeutectoid cementite, as shown by Figs. 28, 29, 37, and 38. Temper carbon was first positively identified in the specimen quenched after 12 hr. annealing (Fig. 31). The presence of temper carbon in the specimen quenched after 8 hr. annealing is extremely doubtful (Fig. 30).

In these, and other observations made by us, the temper carbon in quenched specimens seems to be coincident with the appearance of troostite or martensite. This would seem to signify that no appreciable amount of temper carbon is precipitated until a saturated solution is

[8] O. W. Storey: Researches in Annealing Process for Malleable Castings. *Trans.* Amer. Foundrymen's Assn. (1914) **23**, 460.

[9] *Loc. cit*

[10] Merica and Gurevich: Graphitization of White Cast Iron upon Annealing. *Trans.* (1920) **62**, 509.

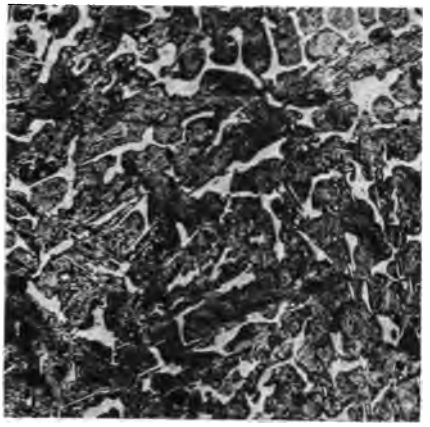

FIG. 28.—QUENCHED AFTER REACHING 800° C. × 100.

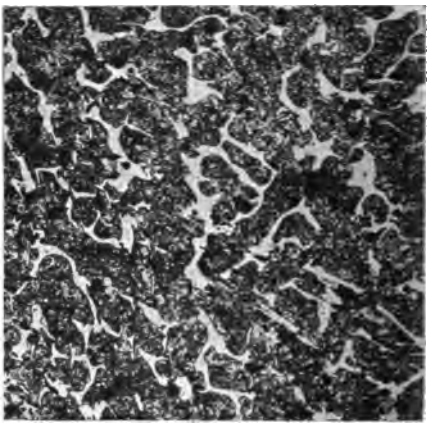

FIG. 29.—QUENCHED AFTER 3 HR. AT 800° C. × 100.

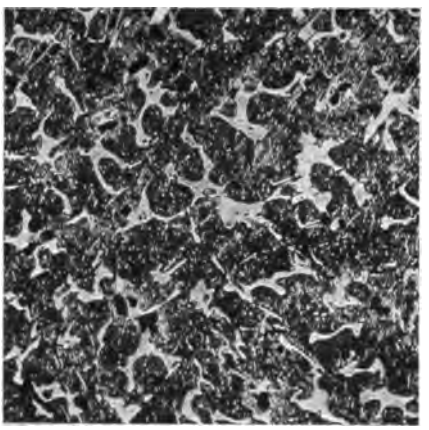

FIG. 30.—QUENCHED AFTER 8 HR. AT 800° C. × 100.

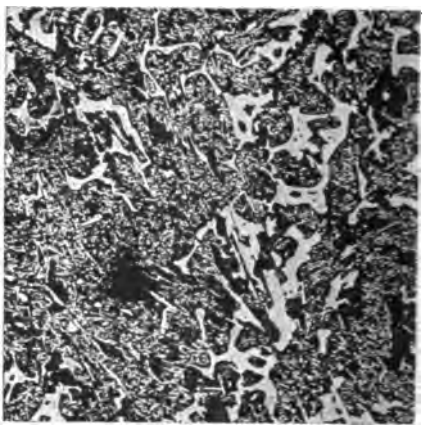

FIG. 31.—QUENCHED AFTER 12 HR. AT 800° C. × 100.

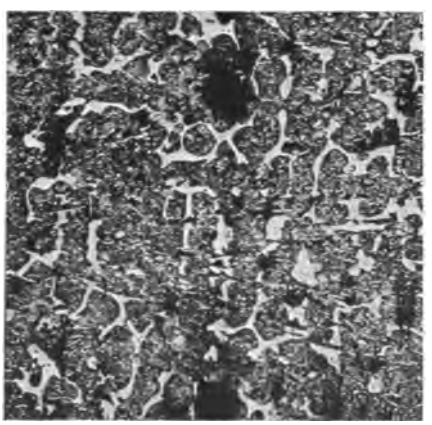

FIG. 32.—QUENCHED AFTER 15 HR. AT 800° C. × 100.

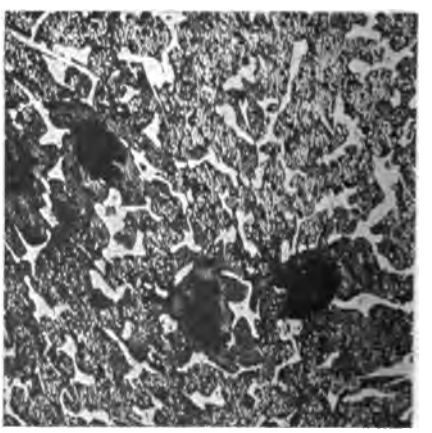

FIG 33.—QUENCHED AFTER 18 HR. AT 800° C. × 100.

SPECIMENS WERE ETCHED WITH 5 PER CENT. NITRIC ACID IN ALCOHOL.

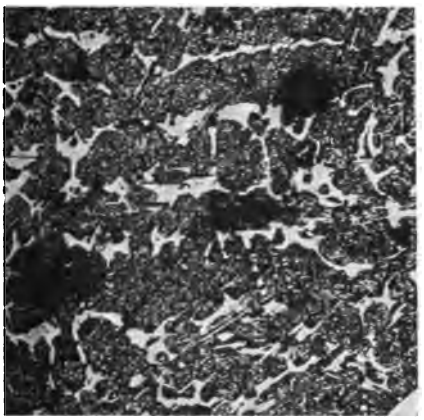

FIG. 34.—QUENCHED AFTER 25 HR. AT 800° C. × 100.

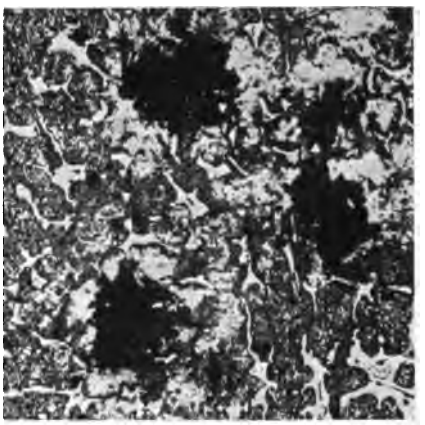

FIG. 35.—QUENCHED AFTER 48 HR. AT 800° C. × 100.

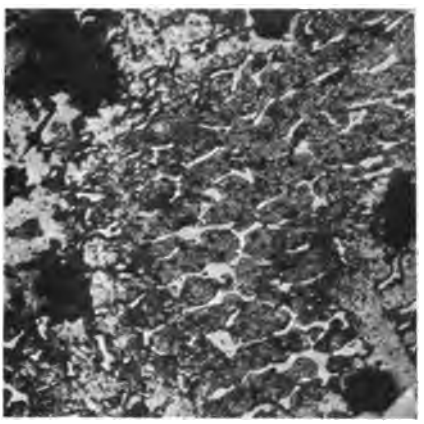

FIG. 36.—QUENCHED AFTER 60 HR. AT 800° C. × 100.

FIG. 37.—QUENCHED AFTER REACHING 800° C. × 1000.

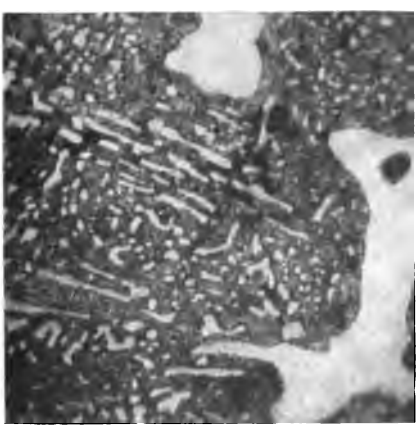

FIG. 38.—QUENCHED AFTER 3 HR. AT 800° C. × 1000.

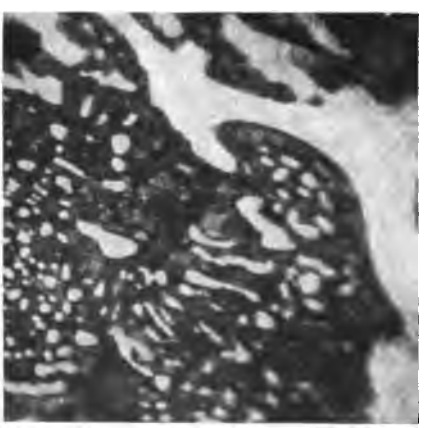

FIG. 39.—QUENCHED AFTER 8 HR. AT 800° C. × 1000.

SPECIMENS WERE ETCHED WITH 5 PER CENT. NITRIC ACID IN ALCOHOL.

FIG. 40.—QUENCHED AFTER 12 HR. AT 800° C. × 1000.

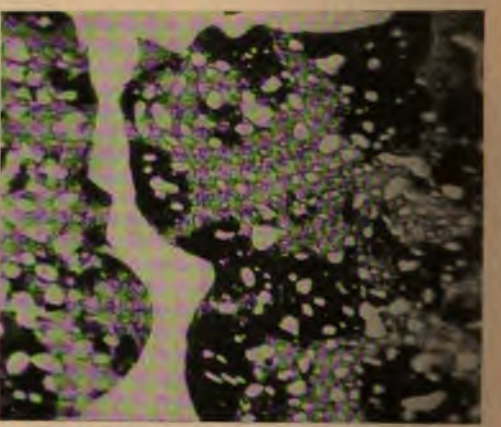

FIG. 41.—QUENCHED AFTER 15 HR. AT 800° C. × 1000

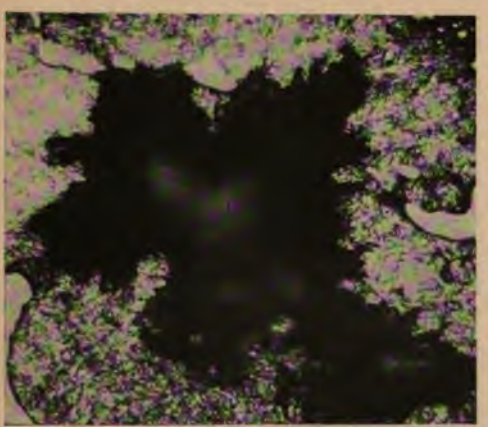

FIG. 42.—QUENCHED AFTER 18 HR. AT 800° C. TEMPER CARBON SPOT IN SOLID SOLUTION AREA. × 600.

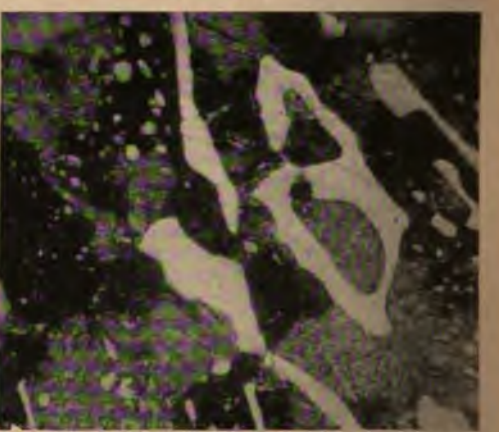

FIG. 43.—QUENCHED AFTER 25 HR. AT 800° C. × 1000.

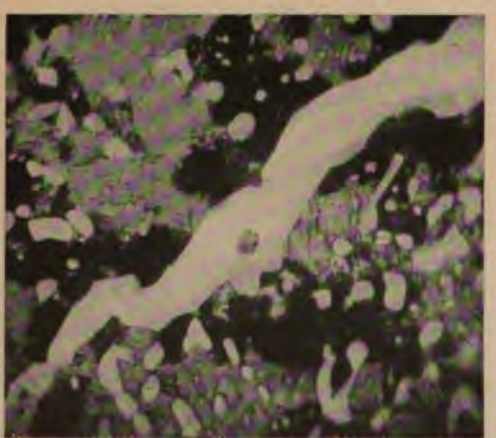

FIG. 44.—QUENCHED AFTER 48 HR. AT 800° C. ×1000.

FIG. 45.—QUENCHED AFTER 60 HR. AT 800° C. × 1000.

SPECIMENS WERE ETCHED WITH 5 PER CENT. NITRIC ACID IN ALCOHOL.

FIG. 46.—QUENCHED AFTER 21 HR. AT 780° C. × 500.

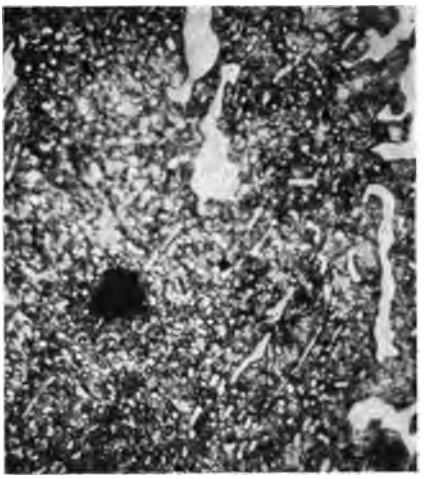

FIG 47.—QUENCHED AFTER 21 HR. AT 780° C. × 500.

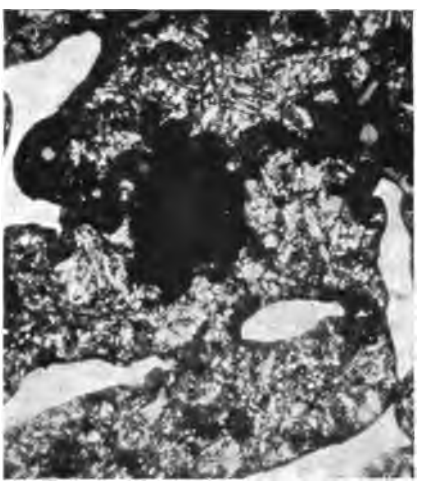

FIG. 48.—QUENCHED AFTER 20 HR. AT 800° C. × 500.

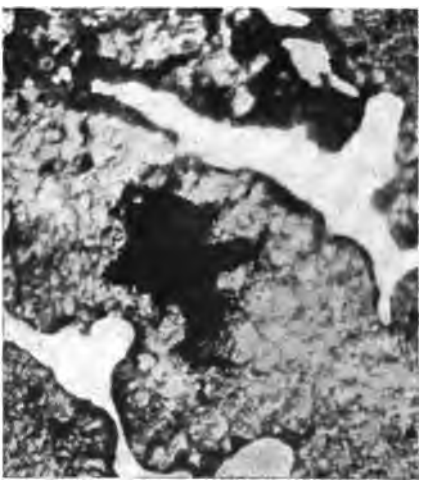

FIG. 49.—QUENCHED AFTER 20 HR. AT 800° C. × 500.

ALL MICROGRAPHS SHOW TEMPER CARBON SPOTS IN SOLID SOLUTION AREAS. SPECIMENS WERE ETCHED WITH 5 PER CENT. NITRIC ACID IN ALCOHOL.

formed. Figs. 39, 40, 41, 43, and 45, representative of quenched specimens highly magnified, show the structure to consist essentially of massive and spheroidized cementite in a matrix of martensite or troostite or a mixture of the two. The dark areas in the matrix (Figs. 41, 43, 44, 45) are troostitic and are not to be mistaken for temper carbon. A typical temper carbon spot at high magnification is shown in Fig. 42; this is apparently embedded in a matrix of fine-grained martensite.

As the time of anneal increases, the size and number of the temper-carbon areas increase, as might be expected. Although it is impossible to make any positive statement regarding the structural element giving birth to temper carbon during the early stages of graphitization, we believe from certain quenched samples, *e.g.*, Figs. 31 to 34, that the temper carbon was first precipitated in appreciable amounts in the solid-solution areas and not, in general, in the patches of massive cementite. As additional evidence we are including four micrographs of two specimens, one quenched after 21 hr. at 780° C. (Figs. 46 and 47) and the other quenched after 20 hr. at 800° C. (Figs. 48 and 49). In the specimens quenched after 25 hr., the temper carbon areas are very bulky; consequently, little can be said regarding the structural conditions prior to graphitization. It is possible, however, that during the later stages of separation some of the massive cementite also undergoes decomposition.

It is not unlikely that slight fluctuations in temperature during the effective annealing period may play an important part in the formation of temper carbon. After the austenite has become saturated with carbon, whether it is in the form of cementite or as atomic carbon,[11] a slight drop in the temperature would render the austenite supersaturated at the lower temperature and carbon would be rejected, apparently as temper carbon. As temper carbon is less soluble than cementite in gamma iron, when the temperature rises the austenite would become saturated at the expense of the structurally free cementite. Thus alternate precipitation and saturation take place throughout the anneal; moreover, further separation of temper carbon takes place during the slow cooling following the anneal since the solubility of carbon in austenite decreases with falling temperature. In properly annealed malleable castings little combined carbon can be found, either analytically or micrographically, and we are inclined to believe that the iron-graphite eutectoid is at approximately zero per cent. carbon.

DISCUSSION

SAMUEL EPSTEIN,* Washington, D. C. (written discussion).—On page 467, the authors say: "The exact temperature at which carbon begins to

[11] As a result of recent investigations by means of the X-ray spectrometer, Jeffries states that "the carbon in austenite is present as individual atoms." *Chem. & Met. Eng.* (1921) **24**, 1057.

* Physical Chemist, Bureau of Standards.

form has been greatly disputed. Some investigators believe that the change is initiated at, or slightly above, the A_1 point; others hold that graphitization can take place below the lower critical temperature. This point will be discussed elsewhere in this paper and some experimental results bearing on the subject will be offered." The discussion of this point and the presentation of the experimental results have been omitted by the authors. However, experiments of a direct and decisive nature

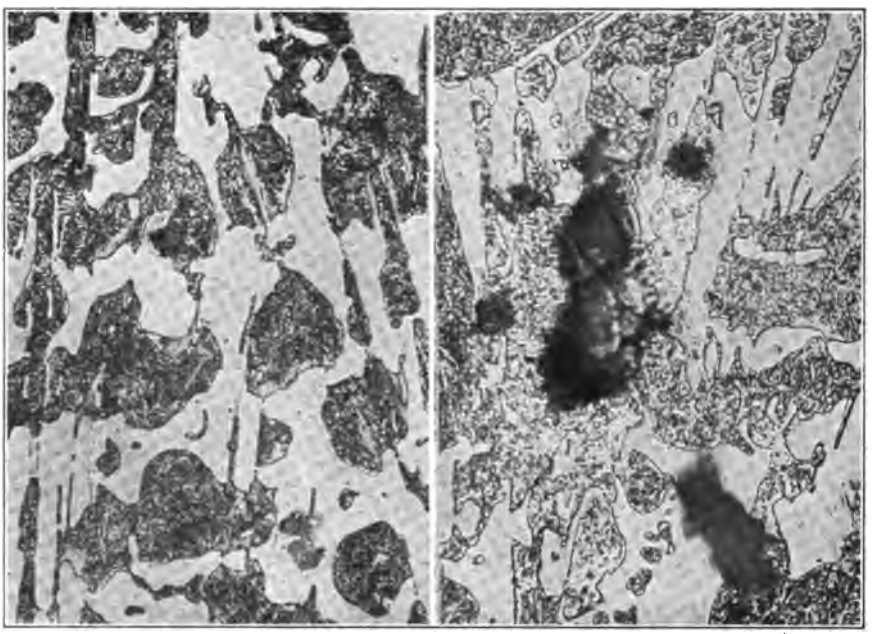

FIG. 50. FIG. 51.

FIG. 50.—WHITE CAST IRON HEATED FOR 288 HR. AT 500° C.

FIG. 51.—WHITE CAST IRON HEATED FOR 288 HR. AT 600° C. ETCHING REAGENT 2 PER CENT. ALCOHOLIC NITRIC ACID. × 500. AFTER HEATING AT 500° C. NO GRAPHITIZATION CAN BE DETECTED BUT AT 600° C. APPRECIABLE AMOUNTS OF GRAPHITE ARE FORMED.

have been carried out by the Bureau of Standards, which it is believed settle this matter definitely. The results show that considerable graphitization takes place after prolonged heating, at temperatures as low as 600° C. in both gray and white cast iron.

Figs. 50 and 51 show photomicrographs of white cast iron heated in an atmosphere of nitrogen for 288 hr. at 500° C. and 600° C., respectively. No graphitization could be detected in the specimen after heating at 500° C. but at 600° C. appreciable amounts of graphite were found to be present; in the gray iron, graphitization at 600° C. is even more pro-

nounced. Fig. 52 shows the extent of graphitization occurring after heating 144 hr. Originally the structure of the matrix consisted of pearlite with large amounts of excess cementite; after heating, the pearlite was removed entirely, having been converted into graphite and ferrite. The thin lamellae of pearlitic cementite were decomposed though the larger masses of hypereutectoid cementite were apparently unaffected. The original compositions of the cast irons were:

	Total Carbon, Per Cent.	Manganese, Per Cent.	Phosphorus, Per Cent.	Sulfur, Per Cent.	Silicon, Per Cent.	Graphitic Carbon, Per Cent.	Combined Carbon, Per Cent.
White cast iron.....	3.39	0.68	0.348	0.171	0.61	0.02	3.37
Gray cast iron.....	3.49	0.66	0.297	0.208	0.63	2.54	0.95

These experiments were conducted primarily for determining the maximum allowable temperature for the annealing, or "pitting," of

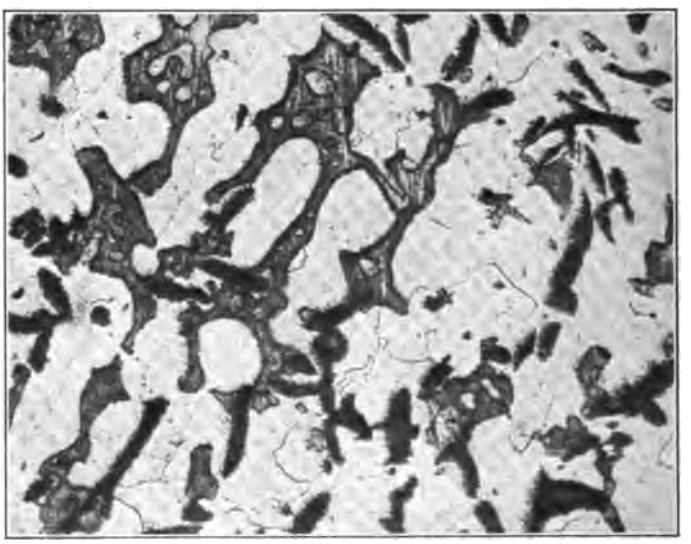

Fig. 52.—Gray cast iron heated for 144 hr. at 600° C. Etched first with 2 per cent. alcoholic nitric acid and then with hot sodium picrate, × 250. The white background is ferrite, in which the grain boundaries are revealed by the 2 per cent. nitric acid etching, the gray masses are cementite which was darkened by the sodium picrate etching, the black plates are graphite. Before heating, the structure of the matrix consisted of pearlite with excess cementite. The pearlitic cementite has been completely graphitized.

cast-iron car wheels. The wheels must be annealed, but there must not be any graphitization of the chilled treads. As has been shown, graphitization occurs after heating for 288 hr. at 600° C., which is more than 100° C. below what is considered themaximum allowable temperature for the annealing of chilled-iron wheels. Of course at 600° C. the time required for graphitization is excessive so that probably the actual practice in the annealing of car wheels need not be changed. Theoretically,

however, the fact that graphitization may take place at temperatures far below the lower critical range is of the utmost importance.

At these temperatures the pearlitic cementite is free, not in solid solution, yet it is partly graphitized in the white iron after 288 hr. and completely graphitized in the gray cast iron after 144 hr. Free cementite, then, may be graphitized directly at a temperature as low as 600° C. Indeed as complete graphitization cannot occur above the A_1 temperature for, as shown by Archer,[12] above that temperature graphite goes into solution, the final stages of graphitization in the malleableizing process must occur below the A_1 point, from the cementite that is precipitated out at that point and therefore not from solid solution. It appears that the reason why the large masses of hypereutectoid cementite are not completely graphitized at the low temperatures is because graphitization, like any other chemical reaction, takes place much more slowly for large bodies, as in the case of the hypereutectoid cementite, than for smaller masses, as in the case of the pearlitic cementite lamellae. At any rate, it seems that in the malleableizing process, where higher temperatures are used, graphitization directly from cementite, that is not from a solid solution, comprises a larger proportion of the total graphitization than the authors apparently suppose. As they must realize, the question of the physical and chemical mechanism of graphitization still remains a problem on which the experimental data are so meager and inconclusive that we cannot do much more than speculate about it. The fact, however, that graphitization may occur at a temperature as low as 600° C. has been proved by direct experiment.

H. A. SCHWARTZ,* Cleveland, Ohio (written discussion).—The writer's critical points, referred to by the authors, are not entitled to too much weight, for at that time a satisfactorily sensitive pyrometer equipment was not available. The determinations were made on a commercial hard iron of, now, unknown composition. Possibly the carbon may have been 2.60 or 2.70 per cent. and the silicon around 0.75 per cent. Determinations were made by the method used by the authors, but counting the peaks as the critical points. Recent precise work in this laboratory would lead us to expect the A_1 point at about 750° C.

While Phillips and Davenport do not stress the point, it is noteworthy that they find Ac_1 in hard iron lower than in malleable; this the writer believes to be a fact, and a part of the work of this laboratory was to confirm the observation that A_1 in the stable system is higher than in the metastable. The writer is gratified that this fact, first demonstrated so far as he knows by his coworkers, is now independently confirmed by the authors. Their Ar_1 point in malleable iron is, we believe, the metastable point; in some of our work, we feel that evidence was found of the existance of the critical points of both systems in the same specimen.

* Research Laboratory, The National Malleable Castings Co.

[12] Graphitization of White Cast Iron. See page 445 *et seq.*

The writer has frequently had occasion to emphasize the identity of temper carbon and graphite; this identity has more recently been confirmed on the basis of radiographic methods by other observers. The geometric distribution is apparently solely dependent on the plasticity, hence on the temperature of the material in which the carbon grows The presence of proeutectic, massive cementite, so characteristic of all white iron, is ably shown to be due to supercooling, forming an interesting and important contribution to our interpretation of micrographs of hard iron. Certain work in progress in this laboratory apparently further elucidates this explanation in the light of the diagram for the ternary system C-Si-Fe.

The principle that graphitization is always initiated in the solid solution and not in the cementite is probably generally accepted; the authors' photomicrographs record the evidence very well. While subscribing to their conclusions the writer cannot forbear to record the observation that cementite, isolated from hard iron, graphitizes very rapidly.

The writer cannot subscribe to the view that "carbon in austenite is present as individual atoms" if this view precludes the possibility of other forms of carbon in the solute. The evidence depends on the apparent existence of two distinct series of solid solutions and is reserved for later independent publication.

A year ago the writer would have received gladly the conclusion that the "the iron-graphite eutectoid is approximately at zero." Recently evidence has accumulated that indicates either that the At_m line (the line in the stable system corresponding to Ac_m in the metastable, *tm* from "temper carbon) either has a sharp inflection just above A_1 or else intersects A_1 at about 0.50 per cent. carbon. A further discussion is withheld for later publication pending further investigation.

The writer calls attention to his paper on effect of machining and of cross-section on the tensile properties of malleable cast iron[13] for physical tests supplementing the authors' conclusions on the effect of thickness of wall sections. It is unfortunate that time did not permit of more accurate work correlating tensile properties with heat treatment. Cooling rates are extremely important variables in this respect; and the fact that this feature was not worked and that anneal was completed only at the higher temperatures rather minimizes the utility of this particular phase of the authors' work.

A. E. WHITE,* Ann Arbor, Mich. (written discussion).—The authors call attention to the apparent lack of complete agreement among various investigators on the true critical points in malleables. Lack of agreement

[13] *Proc.* A. S. T. M. (1920).

* Professor of Chemical Engineering, University of Michigan.

is doubtless caused more by variations in composition and variations in the initial condition of the carbide than by inaccuracies on the part of those making the determinations.

The statement "It has long been known that extremely high temperatures will cause so-called burned castings" is misleading. It is not the high temperature but the oxidizing atmosphere, the activity of which is greatly increased by the high temperature, that results in the production of so-called burned castings; high temperature in a neutral or reducing atmosphere will not produce burned castings.

The temperature record of mill anneal shows how far from ideal is the present box-type furnace, presumably the kind used and without doubt one of the best of its kind. During the "at heat" period, the temperature difference between two different locations in the furnace was never less than 200° F. The time at heat was in one location nearly double that in another, or 150 hr. compared to 85 hr. and the time "to reach heat" was ten times greater in one locatioin that in another, or 50 hr. in the one case compared with 5 hr. in the other. Such conditions do not represent good furnace design; they indicate that the metallurgical operation has been called upon to adapt itself to the design of the furnace employed rather than for the design of the furnace to be based on the service it must render.

The results of the tests in Table 2 indicate the wide latitude possible in the annealing cycle. But for that, attempts to procure closer apprecation of the time conditions which occur in the conversion of white iron to malleable would doubtless have been started earlier. These tests indicate that not only is the metal annealed under the two sets of conditions "of reasonably high quality" but also that there is appreciably little difference between the average quality of the two grades. For some reason or other, though, the samples annealed at the higher temperature seem to be somewhat more uniform.

Tests III through IX present much interesting data. From work done in the laboratories at the University of Michigan, we can confirm the authors' statement that the cause of the partial white fractures in test III was caused by too rapid cooling through the critical range. From 800° C. (1472° F.) to 650° C. (1202° F.), the rate should not exceed 4° C. or 7° F. per hr. The time at heat in both this test and also in test IV is much too long; 4 hr., and probably 2 hr., would have been sufficient. Tests we have conducted also demonstrate that the failure to procure complete malleableization in Tests V, VII, VIII, and IX was the result of holding the samples at the at-heat period too short a time. This period in test V should have been doubled, probably at the very least, and in tests VII, VIII, and IX it should probably have been trebled.

The marked high strength of the samples in test III is undoubtedly due to the combined carbon present. The same explanation holds true

for the high strengths of the bars in tests VII, VIII, and IX. It is unfortunate that no chemical analyses of the bars were submitted, for a much clearer conception of the degree of malleableization could then have been obtained than solely by a metallographic examination.

With reference to the mechanics of graphitization the photomicrographs furnish excellent evidence, supporting the theory that the graphite forms from the carbides in solid solution. In none of the photomicrographs submitted, and in fact in none that the writer has seen, does the graphite give an indication of forming from excess cementite. In Figs. 31 to 36, 42, 46 to 49, the graphite seems to be superimposed on that part of the carbide which, at temperatures above the critical, is in a state of solid solution. In fact, in many of the photomicrographs the graphite seems to have absolutely no contact with the excess cementite. It is appreciated that these conclusions are drawn from studies of two dimensions, whereas that which we are considering is of three dimensions. Yet, since the evidence from the two dimensional angle is sufficiently striking to draw attention, we cannot help but question if we have not before us visual evidence of the nature of the precipitation of the graphite.

R. S. ARCHER, Cleveland, Ohio (written discussion).—The changes involved in the process of converting white iron to malleable iron are, as the authors state, "extremely complicated and not thoroughly understood." They are moreover interesting from the metallographic standpoint, and quite important from the practical standpoint. Of particular interest are the observations that "the ferrite grain size increases with the temperature and probably, with the time of anneal;" and that "the finer the hard-iron structures the finer will be the ferrite grain and temper-carbon areas of the malleable iron." These facts are to be expected, but published evidence of them is lacking.

Evidence is presented in favor of the proposition that the graphite forms directly from solid solution rather than by decomposition of a structurally free cementite. On page 483, it is stated that "the temper carbon in quenched specimens seems to be coincident with the appearance of troostite or martensite. This would seem to signify that no appreciable amount of temper carbon is precipitated until a saturated solution is formed." This is supposedly only after 12 hr. at 800° C. The heating curve of white iron given indicates that the formation of the solid solution was practically completed by the time 800° C. was reached. Furthermore the coarsening of the pearlite lamellae, which was observed before the precipitation of temper carbon, could take place only by precipitation of cementite from a solution supersaturated with respect to particles of this size. The failure to obtain martensite or troostite in some of the specimens can be attributed to the slowness of quenching (in fireclay containers) more reasonably than to incomplete solution.

Like the authors, the writer has tried to determine the source of the initial graphite precipitation by observing the location of the first visible spots. Sometimes these have been in the areas representing the original primary austenite and sometimes they have encroached on the massive cementite; even when they lie completely in the primary austenite areas, there is no evidence that they formed from the solid solution. These areas contain an excess of cementite over the amount soluble at 800° C., as shown in some of the photomicrographs. The graphite may well have formed from these particles which, because of their greater surface area, are probably less stable than the massive cementite.

While the mechanism of the first formation of graphite is still a question, there is little doubt that some graphitization takes place directly from solid solution. The "bull's eye" structure, Fig. 10, consists of a nucleus of temper carbon surrounded by a ring of ferrite, which is in turn bordered by pearlite or sorbite. Long heating below A_1 results in the widening of the ferrite ring and the complete elimination of combined carbon. This process must take place by the diffusion of carbon from the pearlite through the ferrite to the graphite. Small as is the solubility of cementite in ferrite, that of graphite is less, so the cementite dissolves and the carbon is reprecipitated on the graphite. It is not conceivable that the carbon is reprecipitated as cementite on the graphite nucleus, subsequently to decompose, for we would then have a small cementite crystal precipitated from a solution saturated with respect to larger cementite particles and hence undersaturated with respect to the small crystal.

The last sentence says, "In properly annealed malleable castings little combined carbon can be found, either analytically or micrographically, and we are inclined to believe that the iron-graphite eutectoid is at approximately zero per cent. carbon." The writer agrees that the combined carbon content can be reduced to a very small amount, certainly less than 0.05 per cent., but he does not agree that the iron-graphite eutectoid is at or near zero per cent. carbon. In the paper to which the authors refer, the writer reached the conclusion that the iron-graphite eutectoid is practically identical with the iron-cementite eutectoid, and hence near 0.70 per cent. carbon in irons containing approximately 1.0 per cent. silicon. This discrepancy in our views is chiefly due to different interpretations of the term "iron-graphite eutectoid," rather than to different conceptions of the facts. The writer's interpretation is as follows:

In the equilibrium diagram, the iron-graphite eutectoid point is the intersection of the solubility curve of graphite in austenite with the solubility curve of ferrite in austenite. The ferrite curve is exactly the same as in the iron-cementite system, being altered of course by variations in silicon content. For this intersection to come at zero per cent. carbon, the temperature (Ae_1 stable) would have to be at A_3 of a carbonless iron

containing the amount of silicon in question—that is, near 900° C. Heating an annealed iron at any temperature below this would not cause any absorption of graphite, and, conversely, it would be possible to obtain complete graphitization by annealing entirely at temperatures around 850° C. These suppositions are obviously incorrect, so the eutectoid temperature must be well below 900° C. and the carbon content well above zero per cent.

If specimens of completely graphitized iron are heated to successively higher temperatures, beginning at say 700° C., there will be no absorption of carbon until a certain temperature is reached which is the iron-graphite eutectoid temperature, or the Ae_1 point of the iron-graphite system. At this point absorption will begin and, if sufficient time is allowed, will take place to the extent of about 0.70 per cent. carbon. Assuming that this temperature is 750° C., a specimen heated for a long time at 745° C. and quenched would show no combined carbon, whereas a specimen heated for a long time at 755° C. and quenched would show about 0.70 per cent. combined carbon. In other words, the solubility of carbon increases sharply from near zero to some definite and appreciable value, which the writer believes is about 0.70 per cent. The same facts should be brought out by approaching equilibrium from the other direction. That is, a white iron annealed sufficiently long at 755° C. should reach a state of equilibrium in which the combined carbon content is about 0.70 per cent., but if the annealing temperature is 745° C., equilibrium should be reached at practically zero per cent. combined carbon.

This brings out the true significance of the "critical temperature" in connection with malleable castings. This temperature is the Ae_1 point of the iron-graphite system; it lies theoretically above the Ae_1 temperature of the iron-cementite system but probably is practically identical with that temperature; it is important because it is the temperature above which complete graphitization is impossible.

In addition to the results given, in Table 1 and Fig. 6, on the location of the thermal critical points, attention should be called to the values given for silicon steels by Scott and for cast iron by White in discussion of my paper.[14] For two specimens of cast iron, White found Ac_1 at 771° C. and 782° C., and Ar_1 at 737° C. and 743° C. For a steel containing 0.50 per cent. carbon and 0.90 per cent. silicon, Scott's curves show Ac_1 at 760° C., and Ar_1 at 690° C. The writer's conclusions on the subject will be found in his reply to discussion.[15] The following paragraph quoted from this reply offers an explanation of the fact that Ar_1 is usually found at lower temperatures in graphitized irons than in white irons, and of the still lower temperatures found by Scott for hypereutectoid steels:

[14] This vol., p. 453.
[15] This vol., p. 462.

"Schwartz has referred to Bean's values of 727° C. for Ar_1 of an annealed iron and of 746° C. for a corresponding white iron and takes this as evidence that the critical point of the stable system is below that of the metastable. The writer's interpretation of these figures is different. In the first place, the phase change recorded as Ar_1 in the cooling curves is identical in the two irons. If an annealed malleable iron is heated above the critical temperature, part of the graphite goes back into solution; then on cooling at a rate suitable for taking a cooling curve, most of the carbon of this solid solution is precipitated in the form of pearlite. The Ar_1 of the cooling curve is, therefore, the temperature of the pearlite transformation on cooling, whether the specimen is malleable iron or white iron. The fact that Ar_1 occurs at a higher temperature in the white iron is due simply to the presence of an abundance of structurally free cementite nuclei, which are practically absent in the annealed iron. Doctor Howe has shown that the Ar_1 point of a eutectoid steel can be depressed by increasing the maximum temperature to which the steel is heated, because of the more thorough destruction of cementite nuclei. This effect is accentuated in the present case because of the great amount of free cementite in the white iron."

Forgeability of Iron-nickel Alloys

By T. D. Yensen,* M. Sc., E. E., East Pittsburgh, Pa.

(New York Meeting, February, 1920)

In the investigation of the magnetic properties of iron-nickel alloys,[1] it was found necessary in order to make the alloys forgeable, or malleable, to add small quantities of some other element.

Iron-nickel alloys have been known for nearly a century, but have been made in commercial quantities only since 1885. Their remarkable mechanical properties were disclosed by Riley in 1889 and from that time on a large amount of research work has been done both to discover new properties and to correlate the results obtained.[2] Lately the Bureau of Standards has collected the published data in a special circular[3] giving in compact form an account of the properties of the iron-nickel alloys. It also contains a clear historical sketch of the development as well as a selected bibliography.

The chief difficulty with the development of iron-nickel alloys was that the "pure" alloys do not forge readily. The addition of small amounts of manganese, however, made the alloys forgeable, and manganese has therefore come to be regarded as a necessary constituent of nickel steels. The present paper shows to what extent manganese is needed for various nickel contents and also what is the effect of other alloying elements on the forgeability. It also touches upon the cause of forgeability but refers to other sources for more exhaustive treatises on the subject.

The alloys were prepared by melting electrolytic iron and electrolytic nickel with or without other alloying elements in the desired proportions in a magnesia crucible in a vacuum furnace under a pressure of 1 mm. mercury. The ingots, weighing about 2 kg., were allowed to cool in vacuo. If pipes or blowholes were present, the ingots were cut in such

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[1] Paper presented to Amer. Inst. Elec. Engrs. (1920).

[2] The subject has been discussed by Riley (1889), Hopkinson (1890), Osmond (1894 and 1903), Guillaume (1898 and 1903), Dumas (1902 and 1905), and many others.

[3] Invar and Related Nickel Steels, *Circular* 58, U. S. Bureau of Standards (1916).

a way as to eliminate them if possible. Other ingots were also cut in order to give separate test pieces for forging at different temperatures.

The ingots, or pieces of ingots, thus prepared were heated in a coke or gas fire to the desired temperature and forged under a power hammer. On account of the oxidizing condition of the coke fire, there is little, if any, contamination by carbon during the heating. Tests have shown that the carbon content of pure iron thus heated is only 0.01 per cent.,

Specimen No.	Composition				Forgeability			
	Ni %	Mn %	Si %	Ti %	Cold C	Black B	Dull Red D	Bright Br
2Ni203	1.0							
204	1.0		0.2					
207	2.0							
208	2.0		0.2					
211	2.8							
212	2.9		0.2					
213	3.9							
214	3.9		0.2					
215	4.6							
216	4.8		0.2					
217	5.7							
218	5.7		0.2					
219	7.3							
220	7.9		0.2					
221	8.0							
273	8.0	0.1						
272	10.0	0.1	0.2					
223	10.0							
237	9.6							
224	10.0		0.2					
236	9.9			0.2				
225	14.9							
226	15.0		0.2					
247	15.0			0.2				
274	20.0							
248	20.0			0.2				
275	20.0		0.2	0.2				

Specimen No.	Composition								Forgeability				
	Ni %	Al %	C %	Mg %	Mn %	Si %	Ti %		Cold C	Black B	Dull Red D	Bright Br	
2Ni240	20	0.2											
229	25												
230	25					0.2							
249	25						0.2						
241	25	0.2											
231	30												
277	30												
232	30					0.2							
242	30	0.2											
282	33												
283	33				1.0								
233	35												
234	35					0.2							
266	36						0.5						
2105	35				1.0								
2106	35				2.0								
265	36				0.5								
267	36			0.5									
268	50		0.1										
269	50		0.3										
270	50		0.5										
250	50						0.2						
251	50						0.5						
252	50						1.0						
254	50	0.3											
255	50	0.5											

Specimen No.	Composition			Forgeability				
	Ni %	Mn %	Si %	Cold C	Black B	Dull Red D	Bright Br	
2Ni257	50		0.5					
258	50		0.7					
259	50		1.0					
260	50	0.5						
261	50	0.7						
262	50	1.0						
280	50	0.5						
281	50	1.0						
2107	50	1.0						
2108	50	2.0						
263	50	0.5	0.5					
264	50	0.5	0.5					
289	55	0.5						
284	60	0.5						
278	62	0.5						
279	62	1.0						
290	75	0.5						
285	76							
286	80							
291	90	0.5						
292	93	0.5						
287	95							
288	100							
293	100	0.5						

Key to Forgeability

Blank Not determined

None

Poor

Fair

Good

Excellent

FIG. 1.

or practically the same as before heating. If heated in a gas-fired furnace, the iron may absorb 0.01 per cent. carbon during the heating. However, as far as the forging properties are concerned, such a slight contamination is believed to be insignificant and the alloys will be considered as pure iron-nickel alloys except for the additions subsequently recorded.

In Fig. 1, the alloys have been arranged according to nickel content. In most cases the nickel content was obtained by chemical analysis;

in others the added nickel is taken as the nickel content. The figures given for the other elements are the percentages added and not the final composition. In most cases a portion of these elements is lost because of oxidation. The forgeability is visualized by means of shaded squares; the larger the part that is shaded the better is the forging quality.

The forgeability is given for the four conditions: Cold, black heat, dull red, and bright red. Cold means a temperature of 20° to 100° C.; black means any temperature below the appearance of redness, that is below 600°.; dull means 600° to 900°; and bright, temperatures above 900°. These conditions were only estimated by eye, and consequently no great accuracy can be claimed. The forging operation is crude at best, viewed from a scientific standpoint; the temperature begins to decrease as soon as the test piece leaves the fire; and the rate of decrease varies according to (1) the size of the test piece, (2) character of the tongs used, (3) the atmosphere, and (4) the manipulation. Also, the method of forging varies to a large extent; no two blacksmiths will forge alike, and the same blacksmith will forge differently two consecutive test pieces that are alike. In spite of the effort to maintain constant conditions, some variation in the forging quality is undoubtedly due to incidental and personal elements; and on account of the uncertainties thus introduced it would be unwarranted to introduce accurate temperature-measuring devices.

Forgeability of the Iron-nickel Alloys

Up to 7 or 8 per cent. nickel, the forgeability is fairly good at a dull red heat. In the neighborhood of 10 per cent., the forgeability is poor; it is again good for 15 per cent. but poor for 20 per cent., nil for 25, 30 and 35 per cent. (except at a black heat) and up to a high nickel content. Above 75 per cent. nickel, the forgeability is fairly good, and for pure nickel it is good.

The effect of silicon on the forgeability, if any, is very slight. The lower alloys seem to be improved to a slight extent by the addition of 0.2 per cent., but the higher alloys, up to 50 per cent., are unaffected.

Aluminum, carbon and magnesium have no beneficial effect upon the forgeability. If the non-forgeability were due to oxides in the alloys, these elements should have a very beneficial effect because they belong to the strongest deoxidizers known. These results, therefore, indicate definitely that the cause must be of a different character.

Manganese, as was anticipated, makes the alloys forgeable. The 10 per cent. alloy is cured by means of 0.1 per cent. manganese, while the 35- and 50-per cent. alloys require between 0.5 and 1.0 per cent. manganese. A safe formula for 0–50 per cent. nickel would, therefore, be: .

Per cent. manganese required = 2 per cent. of nickel content.

Of all the different elements tried, titanium has the most beneficial

effect upon the forgeability. The amounts required are 0.2 per cent. for 10 per cent. nickel, 0.5 for 36 per cent. nickel, and 0.5 for 50 per cent nickel, indicating that for 0–50 per cent. nickel:

Per cent. of titanium required = 1 per cent. of nickel content.

While this amount will make the alloys forgeable, twice that amount is better. The forgeability of the 10-per cent. alloy was perfect at all forging temperatures with 0.2 per cent. titanium added; this was also the case with the 50-per cent. alloy with 1.0 per cent. titanium added. Consequently a safer formula would be:

Per cent. titanium required = 2 per cent. of nickel content.

For nickel contents above 50 per cent. the data are insufficient to be conclusive, but the indications are that the foregoing formulas may be used by substituting "iron content" for "nickel content;" that is, for 50 to 100 per cent. nickel:

Per cent. manganese required = 2 per cent. of iron content.

Per cent. titanium required = 2 per cent. of iron content.

Microscopic Examination

A number of the forgeable and non-forgeable alloys in ingot form were examined under the microscope in order to discover any possible difference in structure that might explain the different behavior under the hammer. The following alloys were examined.[4]

2 Ni 227, 20 per cent. nickel, non-forgeable.
2 Ni 240, 20 per cent. nickel + 0.2 per cent. aluminum, non-forgeable.
2 Ni 248, 20 per cent. nickel + 0.2 per cent. titanium, forgeable.

2 Ni 250, 50 per cent. nickel + 0.2 per cent. titanium, non-forgeable.
2 Ni 252, 50 per cent. nickel + 1.0 per cent. titanium, forgeable.

The photomicrographs are shown in Figs. 3 to 10, inclusive. While there appears to be a difference in structure between the non-forgeable and forgeable alloys, the difference is not of such a nature as to give any definite answer as to the cause of the variation in the forgeability.

Forgeability versus Non-forgeability[5]

The degree of forgeability depends on the relative strength S_c of the crystals and that of the intercrystalline—or amorphous—material S_i. If

[4] See Appendix 1 for details.

[5] Attention is called to the fact that the manuscript of this paper was prepared prior to the appearance of the paper by Dr. Zay Jeffries, "Effect of Temperature, Deformation and Grain Size on the Mechanical Properties of Metals," presented at the February, 1919, meeting. The author refers to this paper [*Trans.* (1919) **60**, 474] for discussion of the phenomena taking place in deforming metals. It will be noted that the deductions made in the present paper in regard to the criterion of forgeability agree perfectly with those made by Doctor Jeffries, based on a much more elaborate investigation.

the latter is stronger than the former, the crystals will deform when subjected to external forces by slipping along the cleavage planes, and in so doing produce new intercrystalline material along these planes. This, being stronger than the crystals, causes new cleavage planes to be formed with new intercrystalline material, and so on in all directions indefinitely. If, on the other hand, the intercrystalline material is weaker than the crystals, the material cannot be deformed without breaking along the crystal faces; in other words, material with this characteristic is not forgeable. The criterion of forgeability is, therefore, that $S_I > S_c$.

As the relation between S_I and S_c varies with the temperature, a certain material may be forgeable at some temperature and not at others. A measure of the deformability—and therefore to a large extent of the forgeability—can be obtained by means of the elongation and reduction of area upon breaking the material in tension; or in other words, by measuring its ductility. Simple test pieces may be prepared from ingots, castings, or forgings (if available) and tested at various temperatures for elongation and reduction of area. The algebraic mean of these characteristics may then be used as a measure of the forgeability.[6]

In order to test this relationship, the following samples were selected: "Armco" iron, 0 per cent. nickel; 2Ni274, 20 per cent. nickel; 2Ni275, 20 per cent. nickel + 0.2 per cent. titanium; 2Ni277, 30 per cent. nickel. 2Ni274 and 277 were not forgeable except below 500° C., and then only with difficulty, while 275 was forgeable at all temperatures. The ingots were cut into small pieces and forged into rods ½ in. (12.7 mm.) in diameter. From these rods, the test pieces were machined having ½ in. threaded ends and a central portion 1½ in. long by ¼ in. in diameter. The test pieces were annealed in vacuo at 900° before testing, thus giving the material an opportunity to recrystallize. The testing was done on an Olsen 4000-lb., hand-operated, testing machine, the test piece being held by special extension rods at the center of a tube electric furnace, capable of heating the test pieces and adjoining holders to a temperature of 1000° C. The temperature was measured by means of a platinum platinum-rhodium thermocouple directly touching the center of the test piece while it was being tested, thus eliminating any possibility of error in obtaining the temperature.

The results are shown in Table 1 and Fig. 2. The Armco iron—practically pure iron—shows a linear decrease in strength with increasing temperature, while the ductility remains constant up to 500°, probably higher, and drops down to 10 per cent. at 900°. This result, therefore, indicates that pure iron should forge well at a dull red heat and below, but not at higher temperatures. This indication is confirmed by actual facts.

[6] This theory and deductions were developed in conference with Norman B. Pilling.

TABLE 1.—*Mechanical Properties of Iron-nickel Alloys at Various Temperatures*

Specimen No.	Composition		Test-piece No.	Temperature, Deg. C.	Yield Point, Lb. per Sq. In.	Ultimate Strength, Lb. per Sq. In.	Elongation in 1 Inch, Per Cent.	Reduction of Area, Per Cent.	
	Nickel, Per Cent.	Titanium, Per Cent.							
Armco Iron....	0	0	1	20		50,500	40.0	75	
			2	500	22,400	24,600	45.0	75	
			3	900	4,570	4,570	12.5	10	
2Ni 274.....	20	0	A_1	20	50,000	50,000	nil	nil	
			F	20		44,000	nil	nil	
			B_1	300		47,000	nil	nil	
			A_2	500	18,400	18,400	nil	nil	
			B_2	700	12,200	12,200	nil	nil	
			C	900	4,600	4,600	nil	nil	
2Ni 275.....	20	0.2	C	20	64,500	>100,000	?	?	Did not break
			E_1	500	23,500	63,300	20.0	75	
			E_2	700	10,200	20,400	50.0	86	
			F_1	800		9,200	60.0	75	
			F_2	900	5,100	7,800	30.0	61	
			F_3	1,000	4,100	5,600	100.0	94	
2Ni 277.....	30	0	A_1	20	66,500	74,500	nil	nil	
			F_1	300	27,600	45,000	nil	nil	
			D	500	13,300	13,300	nil	nil	
			E	700	9,200	9,200	nil	nil	
			F_2	900	4,270	4,270	nil	nil	

The two nickel alloys without added titanium have very low ductility at all temperatures, the elongation and reduction of area being so low as to be practically zero. The poor forgeability at all temperatures, and particularly at temperatures above 500° is, therefore, in agreement with these results.

The 20-per cent. alloy with 0.2 per cent. titanium added has widely different characteristics. The strength, while decreasing rapidly with increasing temperature, is much greater and the ductility increases with temperature until, at 1000°, both elongation and reduction of area are about 100 per cent. The forgeability should, therefore, increase with the temperature, which was found to be the case, although the alloy forged very well at all temperatures. The 0.2 per cent. titanium has, therefore, entirely changed the characteristics of the 20-per cent. alloy, probably by strengthening the intercrystalline material relatively to that of the crystals. The structures of these alloys were examined by Mr. Pilling and are shown in Figs. 11, 12 and 13.

FIG. 11 (1870–1) and FIG. 12 (1871–1) show the difference in the structure of the non-forgeable 20-per cent. alloy 2Ni274 and the forgeable 20-per cent. alloy, 2Ni275, the only difference in the composition of the two being that the latter contains 0.2 per cent. titanium.

The photomicrographs were obtained from the heads of the tensile test pieces, after the tensile test. FIG. 13 (1872–1) shows, similarly, the structure of the non-forgeable 30-per cent. alloy[7] 2Ni277.

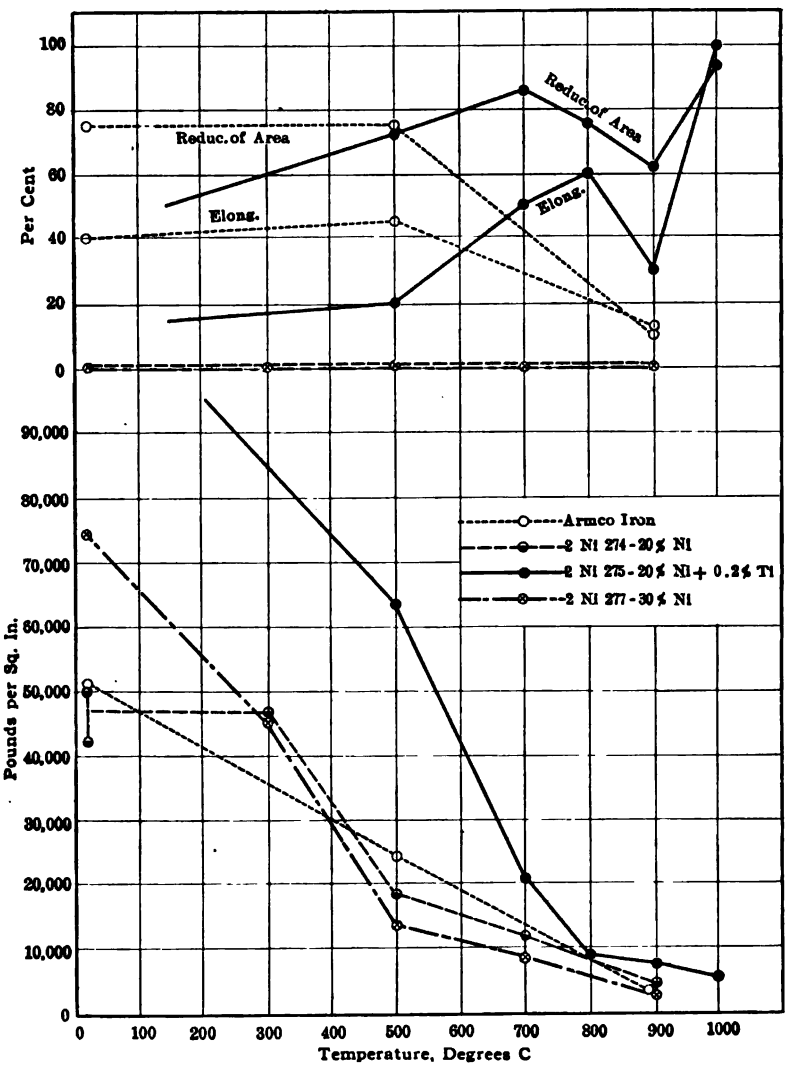

FIG. 2.

[7] Attention is called to the fact that this alloy has not passed the irreversible transformation point, which is below room temperature, and is, therefore, largely in the austenitic, non-magnetic state. However, examination of this alloy after being cooled to −180° C. shows that there is no visible change in the microstructure due to the transformation from the austenitic to the α state. (Magnetic and Electrical Properties of Iron-nickel Alloys, Part II, *Trans.* Amer. Inst. Elec. Engrs., Oct., 1919.)

FIG. 3.—2 NI 227. 20 PER CENT. NI. NON-FORGEABLE. × 75.

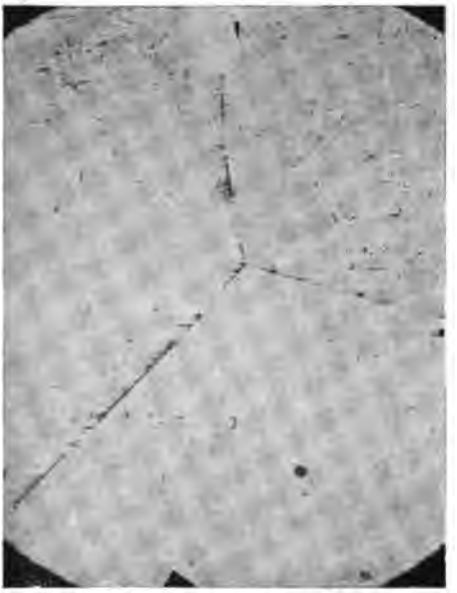

FIG. 4.—2 NI 240. 20 PER CENT. NI + 0.2 PER CENT. AL. NON-FORGEABLE. × 75.

FIG. 5.

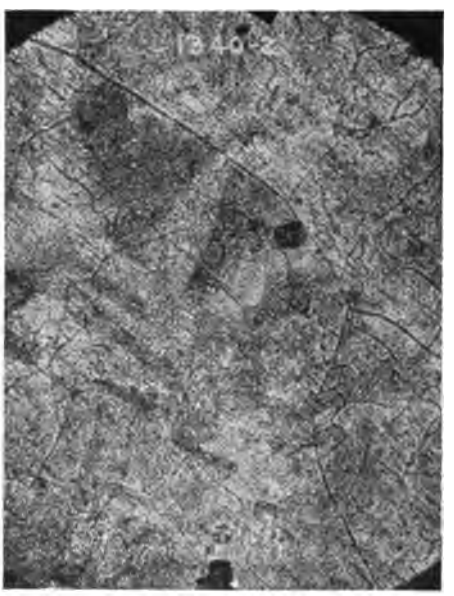

FIG. 6.

2 NI 248. 20 PER CENT. NI + 0.2 PER CENT. TI. FORGEABLE. × 75.

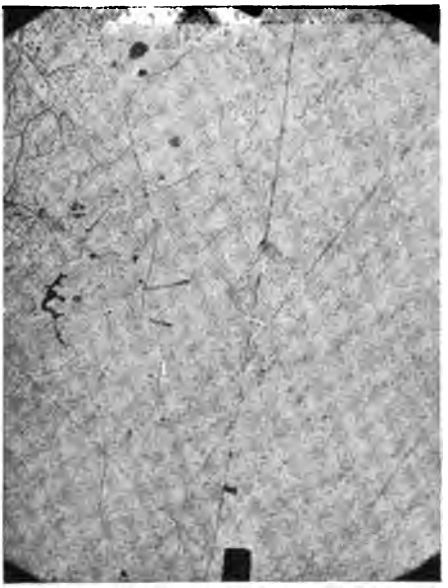

FIG. 7.—× 75.

FIG. 8.—× 375.

2 Ni 250 50 PER CENT. Ni + 0.2 PER CENT. Ti. NON-FORGEABLE.

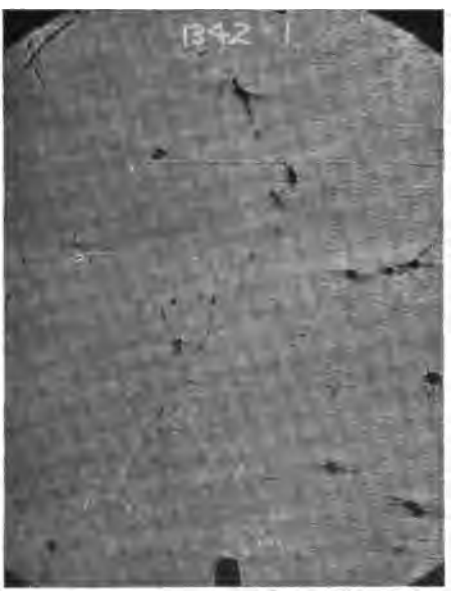

FIG. 9.—× 75.

FIG. 10.—× 375.

2 Ni 252. 50 PER CENT. Ni + 1.0 PER CENT. Ti. FORGEABLE.

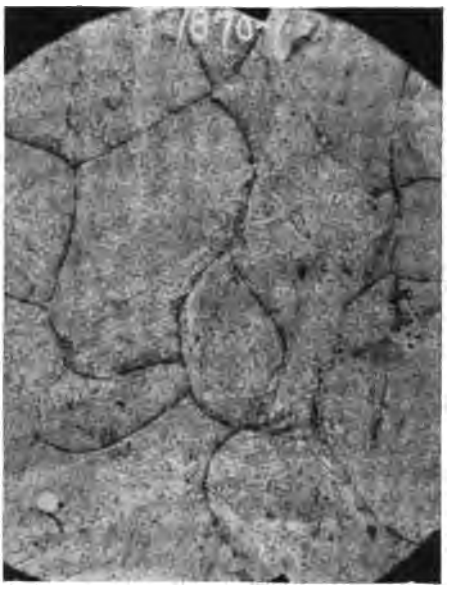

FIG. 11.—2 Ni 274A. 20 PER CENT. Ni. NON-FORGEABLE. × 75.

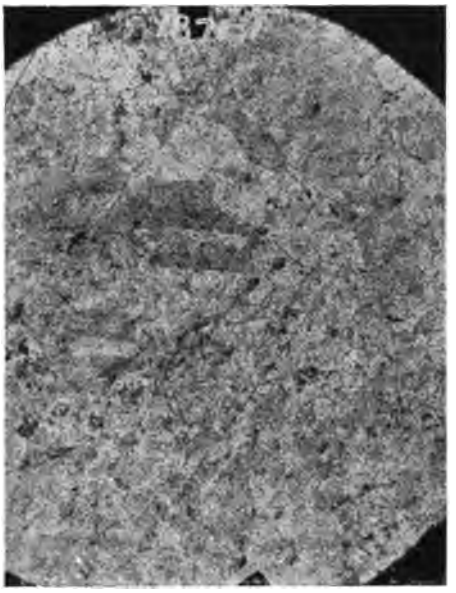

FIG. 12.—2 Ni 275C. 20 PER CENT. Ni + 0.2 PER CENT. Ti. FORGEABLE. × 75.

HEADS OF TENSILE TEST PIECES. ANNEALED AT 1043° C.

FIG 13.—2 Ni 277A. 30 PER CENT. Ni. NON-FORGEABLE. × 75.
HEAD OF TEOSILE TEST PIECE, ANNEALED AT 1043° C.

Summary and Conclusion

1. Pure iron-nickel alloys do not forge readily, if at all, at ordinary forging temperatures.

2. Aluminum, carbon, magnesium, or silicon have little or no effect upon the forgeability.

3. Manganese or titanium in amounts of 2 per cent. of the lesser constituent makes the alloys forgeable.

4. Whereas the degree of forgeability of a material depends on the relative strength of the crystalline and the intercrystalline—or amorphous—material, the forgeability of an ingot or casting can be ascertained only by actually attempting to deform the material, either by forging or rolling, or by a tensile test. Metallography has not yet reached a stage where an inspection of the microstructure will give any definite information in this respect.

5. The fact that manganese and titanium transform iron-nickel alloys from non-forgeable to forgeable alloys means that these elements have the ability to strengthen the amorphous material that is generated between the crystals to such an extent as to make it stronger than the crystalline material.

APPENDIX I

Microscopic Examination of Forgeable and Non-forgeable Iron-nickel Alloys

By Norman B. Pilling

A number of iron-nickel alloys, some of which had and others had not forged well, were supplied for microscopic examination, and from the unforged ingots photomicrographs were prepared; these are shown in Figs. 3 to 10. In all of these alloys, difficulties in etching were experienced; aside from a general inertness toward dilute acids there was a strong tendency to etch rather uniformly, with little contrastive development of details. In all, except the pure iron-nickel alloy, indications of a foreign intercrystalline material were found, the nature of which can only be conjectured from the composition of the addition agents. In all cases where the etching was carried far enough to reveal the grain characteristics, similar structures were found—very large crystals composed in turn of a multitude of angular twinned laminæ. Intercrystalline material, if present, was disclosed long before the general surface etch.

Fig. 3 shows a non-forgeable pure iron-nickel alloy; it shows one grain boundary, which should not be confused with the numerous twinning bands, but no indications of intercrystalline material.

Fig. 4 shows a non-forgeable iron-nickel alloy containing 0.2 per cent. aluminum. The grain boundaries are clearly outlined by a network

of insoluble material, but the actual bulk of this material is extremely slight as the high-power shows; its presence is shown chiefly by the stain surrounding each particle.

The forgeable alloy shown in Fig. 5 contains 0.2 per cent. titanium. After a rather deep etching, each grain was found to be penetrated by a complex system of branching films, similar to those previously observed in certain pure irons. Fig. 6 is slightly out of focus and accentuates this structure. Between the grains themselves a very slight amount of isolated insoluble particles could be found, but by no means in quantities enough to approach a continuous film.

A non-forgeable alloy, containing 50 per cent. nickel and 0.2 per cent. titanium, is shown in Figs. 7 and 8. It has very large grains, each enveloped by a broken film of insoluble material; this intercrystalline material had about 75 per cent. continuity.

A forgeable alloy, containing 50 per cent. nickel and 1 per cent. titanium, is shown in Figs. 9 and 10. Quantities of intercrystalline material are frequently coalesced into relatively large patches at grain corners.

DISCUSSION

COLIN G. FINK,* New York, N. Y.—The speaker had occasion to investigate a series of ferro-nickel alloys some years ago, at which time it was essential to develop a hardness in ferro-nickel equivalent to about that of copper. A composite wire with a nickel-iron core and a copper shell[8] was being made, and unless the core was as soft and as ductile as the shell, the two would not roll down and draw down together.

Samples of high ferro-nickels containing from 20 per cent. to about 60 per cent. nickel were secured from various commercial producers; there was not one that could be called forgeable or ductile; all were so hard that the copper shell would not roll down evenly with the core. After trying out samples of various compositions, to determine which elements in the ferro-nickel alloys caused the rapid hardening during working, it seemed that the one element that was causing the trouble was carbon. By proper heat treatment in an atmosphere of hydrogen the carbon was eliminated and the nickel-iron samples were made so soft that they could be whittled with a jack knife; you would not want ferro-nickel any softer than that. All samples contained manganese; without this, most ferro-nickels break after two or three passes through the rolls.

ZAY JEFFRIES,† Cleveland, Ohio.—I take exception to Mr. Yensen's statement that the intercrystalline cement shall be stronger than the crystals. The term stronger needs definition. Pure lead at ordinary

* Director Research Laboratories, Chile Exploration Co.

[8] British Patent 23775 (1912).

† Director of Research, Aluminum Castings Co.

temperatures is forgeable but it is not ductile; it can be drawn somewhat through dies but not to any great extent. Lead is generally presumed to be non-ductile, because the intercrystalline material is not sufficiently strong to hold together and force the proper load on to the crystals and cause them to deform. Also, copper is quite forgeable at a temperature at which intercrystalline fracture can be produced by tensile fracture. The general statement that the condition for forgeability is that the intercrystalline material shall be stronger than the crystalline, therefore, should be modified.

The statement should also be modified in another respect; namely, the property of the crystal itself must be one that permits of deformation. I do not doubt that fine-grained chromium at room temperature is in such a state of aggregation that the cementing material between grains is stronger than the crystals; yet we could not expect to deform chromium at ordinary temperatures because the crystal itself is not deformable. So the primary conditions for forgeability must include the properties of the crystal itself. First, the crystal itself must be deformable. Second, those crystals must be cemented together with material sufficiently strong to force on the crystals the necessary load to produce deformation.

To define the word stronger, in Mr. Yensen's first statement, the time factor must be considered. Copper, for example, broken in tension with rapid loading at 950° C., breaks through the grains and is quite ductile, as measured by the percentage elongation and percentage of reduction of area. It has a reduction of area of over 99 per cent. in small-wire samples. The same piece of copper, if broken by a slow application of load, will break between the grains without substantial deformation. Therefore, if we modify the word stronger with those ideas in mind we have the general fundamentals for forgeability.

Mr. Yensen gives the tensile properties of these various alloys at higher temperatures. He gives the tensile properties of Armco iron, for example, as approximately 50,000 lb. per sq. in. at ordinary temperatures, and 25,000 lb. per sq. in. at 500° C., and draws a straight line between the two points. It is well known that the tensile strength around 200° to 300° C. is above 60,000 lb.; that is, there is a rise in tensile strength and then a fall to the figure given at 500°. It would be enlightening to have data on the tensile strength of all of these alloys at approximately 100° intervals up to 500°, at least, and then perhaps at larger temperature intervals. Of course, if we could get the results at 50° or 25° intervals, we might obtain even more information.

A. E. WHITE,* Ann Arbor, Mich.—I wish to confirm what Doctor Jeffries has said with reference to the true properties of metals at temperatures between 0° C. and 300° C. Fig. 2 indicates a uniform drop in

* Professor of Chemical Engineering, University of Michigan.

the tensile strength of Armco iron from atmospheric temperature to 900° C. A correct chart would show the tensile strength of Armco iron to reach a peak at approximately 200° C. This same general condition is true with reference to mild steels and wrought iron. Whether it is true with reference to the nickel steels on which Mr. Yensen worked, I cannot say.

Attention is called to these matters for the reason that within the past few weeks I have learned that certain constructing and designing engineers, not familiar with the properties of iron and steel at high temperatures and yet finding it necessary to calculate stresses at high temperatures, have turned to the literature and have been inclined to use such values as are given by Mr. Yensen.

J. W. RICHARDS,* Bethlehem, Pa.—It would make the paper more complete if, on page 503, in addition to other tensile properties the elastic limit of these alloys at various temperatures were given. The range between elastic limit and ultimate tensile strength is a proper measure of the forgeability. In forging, a stress must be put upon the material that is above its elastic limit; therefore the range between the elastic limit and the ultimate tensile strength gives a measure of the forgeability of the material.

I take exception to the statement that elongation and reduction of area, which measure ductility, are a measure of the forgeability. Ductility involves the flowing of the material under slow compression, whereas the forgeability depends essentially on the range between elastic limit and ultimate tensile strength.

The remark has been made that there is a larger field of application of these results, perhaps, to other alloys than the iron-nickel alloys. It is interesting to note that the use of aluminum in steel was preceded by its use in iron-nickel alloys. Marbeau, in France, in 1895, did a great deal of work on making ferro-nickel, which was made in large quantities. He used manganese and some additions of aluminum to deoxidize, and thus obtained a ductile and malleable alloy. For 25 years, I have worn a ferro-nickel watch chain, which illustrates the ductility of the material and also is evidence of its resistance to corrosion. It still retains its original polish, though it has been handled with perspiring hands many thousands of times. The ferro-nickel alloys originating with Marbeau have interesting properties, particularly these anti-corrosive properties under certain conditions. Marbeau used aluminum in the making of ferro-nickel alloys long before anyone thought of using it in steel.

ZAY JEFFRIES.—The evidence given, in the paper, that the fracture is intercrystalline is not conclusive, though this fact is strongly indicated by the films between the grains, which look as if they were non-metallic.

* Professor of Metallurgy, Lehigh University.

The action of the titanium, as shown in Figs. 11 and 12, seems to have broken up this intercrystalline film; but, so far as I can see, that is the only evidence in the paper that the fracture is intercrystalline. It would be enlightening to have some photomicrographs of both sides of the fracture in a number of these samples, showing exactly where the fracture has taken place.

T. D. YENSEN.—In answer to the question as to the effect of carbon, I would say that we started out with practically carbon-free material. Using electrolytic nickel and electrolytic iron, both containing in the neighborhood of 0.02 per cent. carbon, and preparing the alloys under conditions that prevented contamination by carbon, we found that the addition of carbon in various amounts had no appreciable effect.

I took it for granted that in order to be forgeable the crystals had to be deformable; it must be understood that this investigation was incidental to a larger investigation. We were interested chiefly in the magnetic properties of the alloys and had to investigate the forgeability in order to investigate the other. Consequently, we did not feel at liberty to sepnd as much time on this question as we wished to. However, I shall be glad to take up the questions raised by Doctor Jeffries when I return to Pittsburgh, and see what additional information can be obtained.

I realize that the strength of Armco iron, and soft irons generally, increases with the first few hundred degrees rise in temperature. At the time I wrote this paper, I was not as familiar with that particular phase of it as I am now, and, furthermore, we were not so interested in low-temperature characteristics as in the properties at higher temperatures.

With regard to Professor Richards' statement as to the elastic limit, I wish to point out that, in Table 1, the yield point is included. Of course, the yield point is not a very definite quantity, but it may be used as an indication, at least, of the elastic limit. It is interesting to note how the relationship between the yield point and the ultimate strength varies. In regard to the iron-nickel alloy with 0.2 per cent. titanium, there is a large difference between the yield point and the ultimate strength. In one case, the yield point is 23,000 lb. and the ultimate strength is 63,000 lb. per sq. in., bearing out Professor Richards' statement that the forgeability is measured by the difference between these two quantities. However, in the last alloy, at a temperature of 300°, the difference is also large, 45,000 to 27,000 and yet the forgeability is nil. Of course there are possibilities of errors in these quantities and it is possible that Professor Richards' statement holds in all these cases.

COLIN G. FINK.—I would suggest that Mr. Yensen have carbon determinations made of his various samples; it will be quite a revelation

to him to see how much the forgeability and ductility are dependent on the percentage of carbon present. It is impossible to melt ferro-nickel in the carbon vacuum furnace without introducing carbon.

T. D. YENSEN.—Carbon is the element that we have been studying with the utmost care. We have spent considerable time devising methods for determining carbon and have made, I think, more careful carbon determinations than anybody else. We have shown repeatedly that pure iron, melted in the Arsem furnace, contains in the neighborhood of 0.01 per cent. carbon without any further treatment; we have also found only this same quantity of carbon present in iron-nickel alloys and in iron-cobalt alloys, and the variation is only 0.01 per cent. I therefore feel confident that there is practically no contamination by carbon in these alloys.

Mr. Fink believes that the use of the Arsem furnace is *a priori* evidence that the alloys have been contaminated by carbon. I do not know the conditions under which Mr. Fink prepared his alloys, but I believe that some factor aside from the mere fact that he used an Arsem furnace must have been responsible for the carbon contamination.

Casting and Molding Steel Ingots

By Emil Gathmann,* Baltimore, Md.

(Lake Superior Meeting, August, 1920)

Steel as it is poured, or teemed, into the mold for forming the ingot may be broadly separated into two divisions; *i.e.*, effervescing or gassy steel, also termed evolution steel, and non-effervescing or killed steel, also termed solution steel. Between these primary divisions there are various types having the characteristics of both divisions but really not belonging to either; such steels are termed semi-piping, rising, or wild, as the type may be.

True effervescing steel should contain large volumes of gases, which are evolved while the metal is being teemed from the ladle nozzle into the mold, and continue to escape while the temperature of the steel is falling prior to its solidification the top of the ingot remaining liquid, due to the evolution of gases, until an ingot skin of considerable thickness has been formed. These gases consist principally of hydrogen, carbon monoxide, nitrogen, and ammonia. It is generally understood that nitrogen gases are the first evolved and these form the skin blowholes, troublesome at times, in the solidifying ingot.

Ingots made of effervescing steel will always contain a large number of blowholes. Such blowholes are not deemed objectionable in certain products if they occur well inside the ingot where they will not be subject to oxidation upon cooling, reheating, and rolling or forging of the ingot. Very little top or bottom discard is taken from this type of ingot, as pipes, or large shrinkage cavities, at the upper portion of the ingot do not usually occur, the difference in volume between the liquid and the solid steel (6 to 10 per cent.) being compensated by the innumerable blowholes distributed throughout the body of the ingot. Of the 40,000,000 tons of steel made in the United States during the year 1919, at least 35,000,000 tons of ingots were made of gassy or semi-gassy steel.

Killed, or solution, steel is termed true piping steel from the characteristic pipe or shrinkage cavity that usually occurs in the uppermost central portion of the ingot.

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* Vice President and General Manager, Gathmann Engineering Co.

It is well known that the Government's high standard requirements for sound homogeneous steel were met by most steel plants only after they had equipped their mills with especially designed molds and had modified their methods of practice to combine quality with quantity production.

In the usual method of ingot production, when a mold of larger cross-section at the bottom than at the top is used, only one-half, and frequently less than this, of the ingots can be considered as sound; *i.e.*, free from pipe and segregation in the degasified or killed steel and free of so-called surface blowholes and excessive segregation in ingots produced from unkilled or effervescing steel in which, as previously stated, blowholes are not considered objectionable for certain products provided they lie well inside the surface as of the ingot. During the recent war, when tonnage production was as essential to the Government's requirements as quality, metallurgical engineers presented various means and methods whereby tonnage of ingots would not be decreased while their quality was being enhanced. Several of these methods fulfilled the requirements, and the Government's demand for large tonnage of sound steel was, I believe, fully met during the summer of 1918, due in a large measure to the employment of improved methods for ingot molding.

A physically sound steel ingot, strictly classified, must be free from blowholes and segregation as well as pipe, or shrinkage cavity, in that portion of the ingot to be used in the finished product; hence the steel should be so treated in the furnace, ladle, and mold that (division A) piping, or solution, steel will be produced; or, in softer steel (division B) gassy or evolution steel, so that an effervescing heat with deep-seated blowholes in the ingot will be obtained without pipe or shrinkage cavity. The line of demarcation between the harmful and so-called harmless blowholes in steel ingots of type D, which occurs midway between the primary division A and B and of which at present the larger tonnage is made, is difficult to define; hence, ingots made of type D steel should not be used for any product subject to stresses or requiring a smooth surface, as such steel is subject to sudden failure under stresses far below those calculated and deemed safe from chemical composition and test-bar determinations. Steel ingots, the products of which enter into high-grade finished material requiring superior physical characteristics, such as tools, ordnance material, rails, and other shapes subject to heavy stresses, should certainly be always of division A steel and free of all blowholes, even though the chemical composition of the steel is such as is usually expected to weld up blowholes during the rolling or forging processes, *i.e.*, low-carbon steel for special tanks, structural shapes, etc. As is well known, a greater yield of billets or sheets is secured from the ingot, as molded by the old methods, by allowing the formation of blowholes, but this increased yield is undoubtedly obtained at the expense of the

quality of the product. Low-carbon steels of division B containing blowholes, provided these are located well inside the skin of the ingot, undoubtedly answer the buyer's requirements for such purposes as the production of ordinary building shapes, boiler and tank plates, and sheets of various classifications; type D steels should, however, be avoided in important constructions, even though the defects are not apparent from surface inspection.

The usual mill cropping of ingots of divisions A and D, produced in the old-type mold and by the old standard methods, is rarely more than 20 per cent., or just sufficient to square up the bloom, billet, or sheet, and remove the visible piped portion of the ingots, but this certainly does not assure that the remaining 80 per cent. is sound and homogeneous.

The sheets, blooms, or billets made from division B ingots are classified as firsts and seconds, according to the surface conditions. Firsts are usually obtained from the upper half or two-thirds and seconds from the lower half or third of the ingot. It is suggested that the buyer of steel specify the physical condition of the ingot in accordance with the requirements of the finished material. Fewer failures to meet the final specifications will then occur, and a considerable saving will be effected in avoiding the scrapping of the finished or partly finished product.

The physical defects are usually at diametrically opposite portions of the ingots in products made of killed and unkilled classes of steel, in the semi-killed steel defects may occur at any point of the ingot. The behavior during solidification of the two classes of steels when teemed into iron molds is radically different; solidification in the killed steel has been aptly described by Messrs. Howe and Stoughton as a pine-tree or landlocking crystalline growth, while that of the effervescing steel is the so-called onion-skin class; in type D we find an intermingling of the two classes.

Referring, first, to the solidification of an ingot in a metallic mold according to the pine-tree, or landlocking, type of crystallization, it has been found that, to obtain a practically uniform crystalline structure without recurring axial cavities extending deep into the ingot substance below the primary pipe, it is necessary that the cross-section of such ingots be progressively increased from bottom to top of the ingot. In ingots of uniform horizontal cross-section or with a smaller cross-section at the top than at the bottom, bridges of steel crystals will be formed intermittently over the central longitudinal axis of the ingot and shrinkage cavities will occur under such bridges. This fact was not well recognized until quite recently by most makers of solution or killed steel, although advanced and argued by Dr. H. M. Howe and

Bradley Stoughton 15 years ago, and by the writer for the past 10 years. The commercial method of producing ingots with their larger cross-section at the upper portion has now been worked out into a practicable, method suitable for general use without retarding production or materially changing the administrative practice of the steel mill, and is in daily use at a number of high-quality mills in this country. The quantity of big-end-up ingots produced in this country during the year 1919 amounted to approximately 1,000,000 tons gross, including top- and bottom-cast steel.

Abroad, the subject of producing larger yields of sound, homogeneous steel was given serious attention by the steel maker and consumer earlier than in this country, as is shown by the processes used and advocated by Sir Robert Hadfield, in Great Britain, and by others on the Continent. These methods and processes have been thoroughly investigated by our National Bureau of Standards, Department of Commerce, and the writer was recently informed by Dr. S. W. Stratton, Director of the Bureau, that exhaustive tests had been made with the 100 tons of Hadfield ingots imported from England some years ago and rolled in this country, in comparison with ordinary American-made rail ingots, Sir Robert Hadfield having obtained (fortunately for all those interested in the art) our Government's interest in the production of better ingots with a reduced scrap loss. These tests show the superiority of the big-end-up sink-head ingot in a striking manner. Complete reports of this research, "Steel Rails from Various Types of Ingots," the writer has been advised, will soon be issued by the Government. The writer was permitted to inspect the manuscript of this report, and he feels that much of the apathy in America with regard to this important matter will be overcome by a study of this investigation.

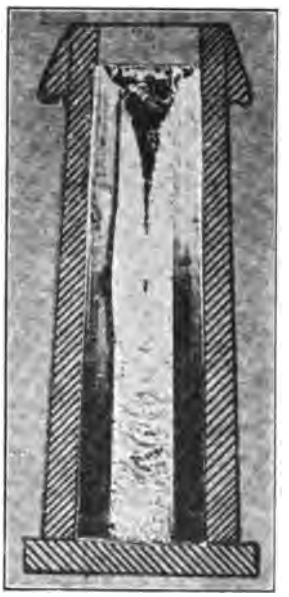

FIG. 1.

Until quite recently, American practice, with some exceptions, was one of tonnage production; and when the buyer specifically insisted upon obtaining really sound, homogeneous steel and was willing to pay a large price therefor, he was usually given the products from the lower half, or possibly third, of the ingot when made of degasified or killed steel, and of the best and cleanest portion (possibly two-thirds) of the ingot when made of open, unkilled or effervescing steel. The remainder of the ingot was sold to customers whose requirements for quality were not so strict, or it was remelted.

Solution steel should, if the specifications permit, have a silicon content of at least 0.20 per cent., as otherwise a large amount of special deoxidizer (aluminum, titanium, or the like) must be used in the ladle and possibly in the mold in order thoroughly to degasify the steel. In effervescing steel, the silicon content should be kept as low as possible and little or no deoxidizer should be used in the ladle or mold, as otherwise a steel of class D will result, having both blowholes and shrinkage cavity, of undetermined location and size.

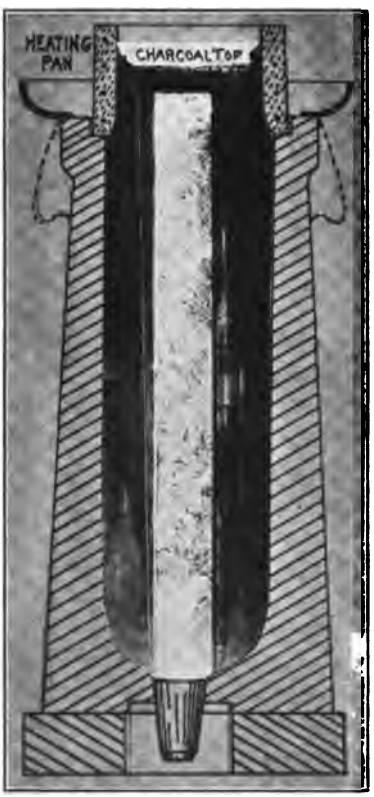

FIG. 2.

Examples of the several divisions of steel are shown in the accompanying illustrations. Fig. 1 is a longitudinal cross-section of a mold of the old standard type showing the ingot structure of division. A dead-killed steel produced therein. Approximately 95 per cent. of the ingot tonnage made in this country is still being cast in molds of this character; the maximum cross-section of the ingot, and hence the larger number of heat units, is at the base of the mold and ingot. Such construction is not correct for molding ingots of killed or solution steel, when a maximum yield of sound, homogeneous steel is desired.

Fig. 2 shows a mold of the new type with larger cross-section and more heat units at the top of the ingot; also the structure produced in a steel of the same analysis and heat as that cast in the old standard-type mold. In the old type, the shrinkage pipe extends to approximately one-half the length of the ingot, while in the improved mold it extends to only approximately 5 per cent. of such length; in both cases, however, blowholes were eliminated, as the steel was thoroughly deoxidized.

The casting temperature, rate of teeming, temperature of molds, etc., considerably influence both the depth of the pipe and the surface conditions in division A steel ingots. The casting temperature and the rate of teeming should be as low as practicable, and the molds should be fairly hot.

Fig. 3 shows an ingote of type D semi-killed steel, in which there is a combination of shrinkage cavity and blowholes, which occur in great

profusion. Steel of this character cannot be improved in soundness by any design of mold as yet devised; the only mechanical method (and this is expensive) for reducing such characteristic defects would appear to be by cross-sectional fluid compression during solidification, as proposed by Illingsworth, Harmot, Talbot, and others. The most feasible method, to my mind, is to cease making this type of steel where soundness and uniformity of product are specified or required, and to use either of the primary divisions A or B, true solution or evolution steels.

FIG. 3.

Fig. 4 shows a longitudinally split ingot of division B steel, a true evolution or nonpiping product, in which a shrinkage cavity is entirely absent and the shrinkage is compensated by numerous, approximately evenly distributed, deep-seated blowholes. In various grades of low-carbon steels, such deep-seated blowholes are not considered harmful, as they are undoubtedly welded by rolling. Segregation is more apt to occur, however, especially in large ingots, with steel of this division, than with dead-killed, or solution, steel.

The best results, as to freedom from surface blowholes, snakes, etc., in evolution steels are obtained when the ingots are bottom cast. This is the practice in the steel plants of our large plate mills. Bottom-casting methods, however, are more expensive than top casting, a loss of approximately 5 per cent. being due to runners and feed head.

Similar results as to deep-seating of blowholes and freedom from snakes have been obtained in division B steel by means of what may be termed top-bottom casting; that is, employing a special pouring nozzle whereby the pressure and velocity of liquid steel as it enters the mold from the ladle are greatly reduced without, however, diminishing the volume of steel teemed per minute. During the war, a variety of apparatus was quite successfully used by various steel producers to accomplish this end. Extensive tests are being made to develop this method of top-bottom teeming further, by reducing the high velocity of the hot stream as it leaves the nozzle of the ladle. It is the general

opinion that division B steel should be teemed near the upper limit of the casting temperature, so that a large volume of gas may be evolved from the ingot, which is the reverse of the practice for killed steel.

It was found necessary, during the war, to improve the quality of the steel ingot and decrease scrap losses in order to meet the large demand for finished product. To obtain a large economy as well as improve the quality of steel product, the highest possible percentage of the ingot should be of such physical condition that it can be worked into homogeneous finished shapes or sections, thus reducing scrap losses with consequent unnecessary fuel and labor waste in continuous remelting operations. Each per cent. increase in sound, usable ingot will effect a net annual saving of over 500,000 tons of coal, coke, or equivalent fuel to the steel industry of our country. The total annual monetary saving for each per cent. increase in finished product will amount to approximately $10,000,000, without considering the manifest advantages and benefits to the public in being able to obtain a better, more uniform product that is capable of giving a longer service for an initial investment.

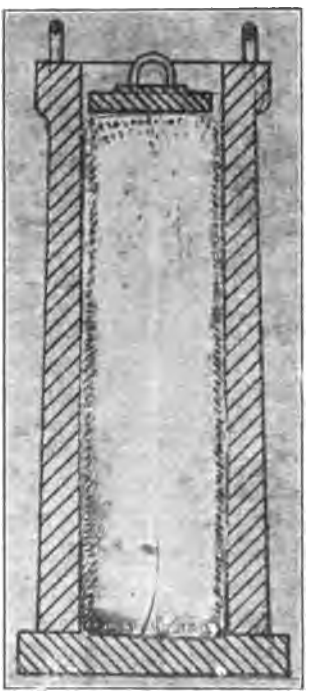

FIG. 4.

While some metallurgists, engineers, and steel producers may possibly not agree with the author in his primary classification of molten steels and the types of ingots formed therefrom, all will agree (academically at least) that more thought and effort should be given to the improvement of the steel ingot, both as to its interior and its surface conditions. This improvement, it has been shown, can be made by suitable molding methods and appliances whereby 80 to 90 per cent. of division A ingot is obtained in sound blooms and billets substantially homogeneous and with good surface conditions.

As the foundation of all finished (mill or forge) steel products is the ingot, its physical and chemical conditions determine the condition of the finished product. In the prevention, or rather reduction, of segregation, especially of division B steel in large ingots, much remains yet to be accomplished.

DISCUSSION

JOS. W. RICHARDS,* BETHLEHEM, PA.—It is undeniable that some of the gases given off by molten steel, as it cools, exist in the steel as dis-

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solved gases, but most of the gases evolved are formed by the reaction of metallic oxides on the carbon present. This evolution of gas can be stopped by using reagents which remove the dissolved metallic oxides.

There is no such thing as a harmless blowhole. The proper thing to do, metallurgically, is to deoxidize the steel completely so that there will be no blowholes, and then to cast it so that there will be no pipe. The problem for steel casters is not the avoidance of dead-melted steel but its proper casting so as to avoid piping. Mr. Gathmann has directed his efforts toward securing the latter result.

EMIL GATHMANN (author's reply to discussion).—Professor Richards has clearly stated the primary requirements for obtaining soundness in steel ingots; viz., "to deoxidize the steel completely so that there will be no blowholes and then to cast it so that there will be no pipe." To fulfill these requirements should be the ideal of all steel producers. That all steel in going from the molten to the solid has volumetric shrinkage is well known to metallurgists but this fact is ignored by many steel casters and molders.

It is possible to control the solidification so that all of this volumetric shrinkage can be confined to the upper 10 per cent., by weight, of the ingot; the writer and his associate, George Dornin, at various steel plants, have so controlled this shrinkage that all was contained in the upper 2 per cent. of the ingot. When this small part, plus a small percentage for the elimination of segregation, has been cropped and discarded, the remainder of the ingot is sound unless easily preventable mistakes have been made. Surface defects, seams, etc., found in a bloom or billet made of dead-melted or deoxidized steel, may be chipped out, with the assurance that they will not reappear in later manufacture. They are here a local surface trouble, while if the bloom is made of gassy, or so-called effervescing, steel, new seams may continue to appear by the opening of the remains of blowholes as long as the steel is heated or worked, as they are here due to internal conditions.

To get sound steel commercially, it is necessary to cast the ingot with its large end up, so that the pipe will be of the open, or primary, type which is capable of being fed, and to use a refractory sink head or feeder to do this feeding. The ingot must also be allowed to solidify completely before rolling.

Many steel makers are afraid of a deoxidized, or dead-melted, steel because of pipe. If they could only see how simple the control of pipe is and how utterly impossible it is to make steel sound or of good quality without making it pipe, they would no longer fear this condition.

Professor Richards says: "The problem for steel casters is not the avoidance of a dead-melted steel, but its proper casting so as to avoid

pipe." It is to add to the published data on this subject, in an effort to show how simple and effective are the means now at our disposal for the accomplishment of this object, that this paper has been written. So effective are these means that reliably sound steel can be produced today at less cost than unsound steel.

Making a 5-per cent. Nickel-cast-iron Alloy in an Electric Furnace

By D. N. Witman,* Trafford, Pa.

(Wilkes-Barre Meeting, September, 1921)

One of the special uses to which the electric furnace has been put recently is the melting of an alloy of nickel and cast iron for the production of electrical-resistance grids. The metal sections of these grids, Fig. 1, are quite uniform for each pattern, but there is, among the various patterns, a variety of thicknesses. The cross-sections vary from $\frac{1}{2}$ by $\frac{3}{16}$ in. to as small as $\frac{1}{8}$ by $\frac{1}{8}$ in. The electrical resistance of a perfect casting lies within 10 per cent. above or below the fixed listed resistance for each pattern. Good molding is essential to success in the making of these grids, for with absolutely correct metal, a variation of 0.01 in. in width and thickness of section on some of the patterns may mean as much as 12 or 14 per cent. variation in resistance.

The service for which these castings are intended demands that the metal, even in the smallest castings, be very soft, showing an open, gray, highly graphitic structure, in order that they may be resistant to shock, and stand up well under rough usage. The metal used for this purpose is a gray iron alloyed with 4 to 5 per cent. of nickel, which element, when the composition of the alloy is correct, imparts toughness and pliability to the metal and helps to overcome the tendency of metal to run white and become brittle because of the rapid cooling action of the sand mold. When cold, these castings can be twisted into various shapes, taking a permanent set without breaking. The alloy has approximately double the electrical resistance of ordinary cast iron. The metal specification is as follows:

	Per Cent.
Silicon	2.40 to 2.60
Sulfur	Under 0.05
Phosphorus	Under 0.08
Manganese	Under 0.40
Total carbon	3.60 to 4.00
Nickel	4.00 to 5.00
Copper	0.50 to 0.70

* Metallurgist, Westinghouse Electric & Mfg. Co.

Following are the analyses of three heats showing a normal resistance:

	1 Per Cent.	2 Per Cent.	3 Per Cent.
Silicon	2.40	2.48	2.47
Sulfur	0.010	0.013	0.018
Phosphorus	0.055	0.055	0.074
Manganese	0.13	0.08	0.10
Total carbon	3.92	3.92	3.82
Nickel	4.47	4.24	4.55
Copper	0.67	0.67	0.67

Owing to the uniform results obtained on most of the elements, silicon and carbon only are determined as a matter of routine, with an occasional complete analysis.

On account of the nickel content of the metal, which raises the setting point of the alloy considerably above that for cast iron, causing the alloy to be sluggish at a temperature at which cast iron would have great fluidity, it is necessary to cast at a much higher temperature than would be required for cast iron. The temperature of the metal in the ladle, as determined by a Leeds & Northrup optical pyrometer, runs between 2800° and 2900° F. (1537° to 1592° C.).

The urgency of the situation made necessary the use, largely, of such materials as happened to be in stock in our works; consequently much of the equipment is crude. The furnace is three-phase, combined open-arc resistance type, without bottom electrode, is stationary, and of 1000 lb. capacity. The hearth is built of magnesite brick and grain magnesite while the roof is made of special fireclay brick. Alternating current is delivered by the power company at 22,000 volts. It is stepped down to 220 volts in three 150-kv.-a. single-phase, Westinghouse, lighting transformers, and further reduced to 90 or 110 volts in three autotransformers. These transformers, while not intended for electric-furnace use, have stood up remarkably well, having at times carried an overload of more than 100 per cent. for an hour. Four-inch Acheson graphite electrodes are used, and the regulation is by hand. A switchboard, located in a convenient place for the furnace operator, contains a voltmeter, three ammeters, and the power switch.

The required amounts of pig iron, scrap, and nickel ingot, together with some retort carbon, are charged into the furnace, the power turned on, and the melting done as quickly as possible. The melting down is carried on at the higher of the two possible voltages, viz., 110-volt, and the input of current fluctuates from 0 to 3000 amp. per phase; the melting requires about 1 hr. to 1 hr. and 10 min. If there is an accumulation of slag on the metal, because dirty metals were used in the charge or because some of the bottom has come up, it is skimmed off. No attempt has been made to use a slag during the melting or the adjusting periods and no unu-

sual difficulties are encountered by reason of the absence of slag, but there may be greater surges of the current than there would be when melting under a slag.

As there is not enough time to allow for chemical determinations, the necessary adjustments are made from observations of test pieces so shaped as to indicate the character of the metal as cast in all sections from a feather edge up to ½ in. Several of these test pieces are cast in sand during the adjusting and heating period, and additions of silicon and carbon are made until the fracture of the test piece shows the metal to be normal. The silicon is added in the form of 50-per cent. ferro-alloy, and

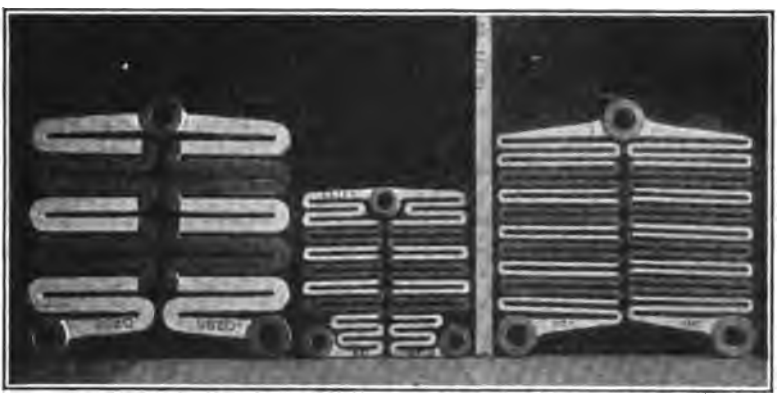

FIG. 1.—ELECTRICAL RESISTANCE GRIDS.

the carbon, in the form of finely ground retort carbon, is thrown over the clean surface of the metal. Tests are then made for temperature both by the use of the optical pyrometer on the metal in the furnace and by taking a spoonful of the metal and noting the time that elapses before it skims over. As stated before, the temperature, to permit running of the smallest grids, should be from 2800° to 2900° F. in the ladle. The adjusting and superheating of the metal requires from 30 to 40 min., thus making the time of the heat from 1½ to 2 hours.

One of the peculiarities of this alloy of cast iron and nickel is a rejection of graphite from the metal when it is just melted, but when the metal is superheated, it again takes up the carbon thrown out at a lower temperature. It is this property of nickel, throwing out graphite on cooling, that helps to make the grids soft and gray in the smaller sections and incidentally keeps the electrical resistance high.

The average power consumption, covering a 9-month period of operation, was 1100 kw.-hr. per ton, while the electrode consumption for the same period averaged 28 lb. per ton. These figures are rather high even for such a small furnace, but considering that the operation was, in a

sense, experimental, and the installation more or less a makeshift, it is probably not as bad as the figures would seem to indicate. With an ideal installation, consisting of a tilting furnace, suitable furnace transformers, and automatic regulation, it would be possible to reduce the current consumption by reason of having a smoother operation, greatly lessen electrode consumption by having less breakage, shorten the time of the heat considerably, reduce the amount of labor necessary to operate the furnace, and thereby decrease the cost of metal in the ladle.

The advantages of this method of melting may be stated briefly as follows:

There is no picking up of sulfur in the melting process; therefore all of the scrap alloy, such as gates, sprues, defective grids, and over iron can be charged back into the furnace and nothing wasted. In fact, it is quite possible and just as easy to run a heat of 100 per cent. scrap as it is to run one made up of pig iron, scrap, and nickel.

The possibility of adjusting the metal to the proper composition while it is in the furnace.

The attaining of the high temperature necessary to cast the metal into very small sections so that it will run clean, and remain gray and tough.

Use of Microscope in Malleable-iron Industry

By Enrique Touceda, Albany, N. Y.

(New York Meeting, February, 1920)

As in the case of steel and the non-ferrous alloys in general, the use of the microscope in connection with the manufacture of malleable cast iron has proved of inestimable value to the industry. Had its use not been invoked, many facts either would not be known at all or, if suspected, would be confined to the realms of conjecture. No fairer statement could be made than that the start of real progress in the industry was coincident with the application of metallography to the product, though the full significance of this statement can hardly be appreciated except by those who not only are conversant with conditions as they existed at the time referred to, but are familiar with the character of works' practice at the present time.

A few years ago, about the only test made to ascertain the physical properties of the product, except in the case of certain plants, was the bending of a casting to destruction, not only with the object of discovering whether or not the metal was ductile, but for the purpose of inspecting the fracture. The characteristics of the fracture, if correctly interpreted, were known to be of value in locating the trouble in castings that were inferior. In general, it was found that if a casting of medium or heavy section would bend through a wide angle before failure took place, the fracture in the majority of cases would have a black velvety appearance; while if it was held at different angles to the direction of the rays of light, it would show a change of color and an iridescent sheen. But an inferior air-furnace heat or anneal might yield castings which, if thin and consequently largely decarburized, could be bent double on themselves and still not possess the fracture described. If, on the other hand, a casting broke short, its fracture might have one of a great many different color and structural peculiarities. Depending on the cause of the trouble, such castings might have any of the fracture characteristics, of which the following is but a partial list.

A uniform lusterless black color throughout, except at the decarburized border.

A uniform steely appearance throughout, there being quite a variety of fractures under this classification from a very white to a grayish color.

A coarsely granular steely border of varying depth, melting gradually into a core of much darker color.

A dark, mouse-colored sparkling fracture throughout, except where decarburized at surface.

A black sparkling fracture throughout, except at decarburized surface.

A steely border, sometimes very granular and at other times of porcelainic texture of varying depth, having a sharp line of demarcation between it and the core contained within it.

A light or dark dove-colored border of varying depth, having a sharp line of demarcation between it and the core that it surrounds.

A black border surrounding a steely white core, a sharp line of demarcation dividing the two.

The foregoing descriptions have been given principally to make clear that it was the invariable custom to inspect carefully the fracture of any broken casting. When the pots were withdrawn from an annealing oven and dumped, various castings were selected for the bending test. If any broke short, the annealer and melter and, perhaps, the superintendent, would try to locate the cause of the trouble. But it was seldom that any two of the men were in accord as to why ductility was lacking or what corrective measure might rectify the condition. The annealer would endeavor to shift the responsibility to the melter, while the latter would complacently state and insist that inasmuch as the hard-iron castings were similar in all particulars to previous air-furnace heats that had but recently annealed in a satisfactory manner, it was plain that the trouble was that the castings had been under or over annealed, etc. The consultation would invariably end with nothing definite being determined because the opinion given in each case was unaccompanied by tangible proof. Matters were rendered more uncertain and further complicated, by reason of the fact that the castings from three or four air-furnace heats are annealed together in the same oven; it is impractical to keep the castings from the various heats separated, for which reason the air-furnace heat to which belonged the casting under discussion cannot be identified.

The writer has been associated with the manufacture of malleable-iron castings since 1894. In 1904, he became convinced that while practical experience combined with close observation, when accompanied by a good metallurgical foundation, made possible the explanation and elimination of many of the troubles encountered, works' control could never be satisfactorily attained without proper facilities for a study of the structure rather than the fracture of the annealed product. Steps were then taken to secure the best metallographic outfit available and, with the aid of a small electric-resistance annealing furnace and this outfit, more knowledge was obtained in 3 months than in the previous 10 years. Toward the end of 1911, the writer was engaged by the American Malleable Castings Assn. as its consulting engineer. At that time, few, if any, of the members suspected that the microscope could be used as an aid in

their work. Today, not only are many of the members equipped with a metallographic outfit, but those who are not make constant use of the one installed in the general laboratories of the association.

Structural Characteristics of Malleable-iron Castings

As a partial list of fracture characteristics has been given, it is pertinent at this point to make a similar one covering the various structural characteristics that are encountered from time to time. This will necessitate a division of the list into two classes, which must be considered separately for the reason that an anneal may be conducted with most painstaking care and precaution and the castings have an abnormal fracture and structure, in the event that the composition of the hard-iron castings is such as to inhibit, in part or almost wholly, the breaking up of the carbides; while on the other hand the hard-iron composition may be the most desirable, and an abnormal structure result solely from failure to observe those conditions vital to a correct anneal. If a hard-iron casting of correct composition is efficiently annealed, its structure will consist of a ground mass of ferrite, throughout which will be quite uniformly distributed a number of fairly well rounded nodules of free carbon. The fewer the number and the smaller the nodules, the greater will be the ductility of the metal.

Irrespective of whether the castings have been placed in an active packing, one containing a certain percentage of iron oxide, or in one that is inactive, such as ashes, sand, ground firebrick, etc., there will always be found a surface border in the section that has been almost completely decarburized, of a depth that will vary from one that is hardly noticeable to one that will at times exceed $\frac{1}{16}$ in. The writer believes the foregoing to cover what can be considered a perfectly normal structure for annealed malleable cast iron, although if a slight outer layer of pearlite is found, surrounding an inner ring or layer of ferrite that is located between the former and the metal enclosed within these two layers, or if the position of the ferritic and pearlitic layers is reversed, the structure should still be considered normal under the assumption that the pearlitic layer, irrespective of location, is not high enough in carbon to make machining difficult.

Structural Characteristics of Improperly Annealed Castings of Suitable Hard-iron Composition

A ground mass of ferrite—particles of free carbon distributed quite uniformly throughout—associated with a small amount or, at times, a great abundance of free cementite, indicates that the annealer failed to raise and hold the oven to a temperature in excess of the critical, or that the casting was not held long enough above the critical temperature to accomplish completely the breaking up of the carbides.

The presence in the ground mass of considerable pearlite, with rings of ferrite surrounding the particles of free carbon, indicates too quick cooling through the critical

range. If these characteristics are confined toward the outer portion of the section, the rate of cooling was but slightly too rapid; if they exist throughout the section the cooling was much too rapid.

A structure normal in all particulars except for the presence of an outer rim of pearlite, corresponding to a steel of from 0.60 to 0.85 per cent. carbon, contaminated at times by the presence of considerable free cementite, indicates the presence of a carburizing atmosphere in the pot.

Structural Characteristics of Properly Annealed Castings that Show Abnormal Structures Due to an Incorrect Hard-iron Composition

A fairly uniform ground-mass mixture of ferrite and pearlite, throughout which are quite uniformly distributed particles of free carbon, indicates very low silicon or manganese or both.

A ground mass of pearlite throughout which are quite uniformly distributed particles of free carbon indicates very high manganese.

A ground-mass mixture of ferrite and pearlite, surrounding which is a layer of pearlite and surrounding the latter a ring of decarburized metal, may be caused by a number of conditions.

A ground mass containing more or less primary graphite indicates that the hard iron was contaminated with uncombined carbon.

Value of Microscope in Malleable-iron Industry

Up to a comparatively few years ago a diagnosis of the fracture was the chief means employed for determining the cause for the superiority or inferiority of the metal in the castings, and as, for the same hard-iron composition, the appearance of the fracture will vary to a considerable extent, the higher the temperature of anneal, the diagnoses were frequently incorrect. The writer knows of no metallurgical industry in which the use of the microscope has proved so indispensable as in the manufacture of malleable-iron castings. He is also positive that there are many troubles, the exact cause of which cannot be definitely located without its aid.

It must not be assumed however, that in all cases dependence on the use of this instrument alone will disclose the true and complete story, for what may be shown by the fracture, the structure, and the chemical composition must, in many instances, be carefully considered too before an accurate diagnosis can be rendered. For example, consider the case in which the hard-iron composition of a casting yields, when annealed in accordance with best practice, a perfectly normal structure but an abnormal fracture. Such cases were of very frequent occurrence in the past and, doubtless, are not infrequent today. When certain constituents are present in the iron in certain amounts, they can affect the ductility of the ground mass without having any appreciable effect in preventing the complete graphitization of the carbon during the anneal; and when the ductility of the ferrite is lessened, a more or less granular and grayish or steely fracture will result, for the ferritic grains instead of stretching out in spines will break short, producing facets that will reflect light and yield

the appearance indicated. Obviously, then, if a person received a micrograph accompanied by a statement that it was truly typical of the structure and he was requested, from its inspection, to pass upon the physical properties of the casting, he would be forced to confine himself strictly to the general statement, that while it could be determined from the micrograph that the anneal had been conducted in accordance with good practice, because graphitization was complete and the grain size good, no prognostication as to physical properties could be vouchsafed unless information concerning the fracture characteristics, or the chemical composition, or both, was furnished.

On the other hand, quite numerous are the cases in which the microscope plays the dominant role. There are certain defects, the nature of which can be revealed only through metallographic means. The presence of slag, of primary graphite, the structural characteristics of the ground mass, the conditions that manifest themselves in the fracture arising from an unsuitable pot atmosphere, whether or not an area seen in the fracture, through contrast, to be different in appearance from the rest of the section is the result of segregation, or is due to some other cause, such as a slight shrink, etc., are impossible of identification in any manner known to the writer other than through microscopic investigation. In the opinion of the writer the use of the microscope in the malleable iron industry is mandatory.

Thacher Molding Process for Propeller Wheels and Blades

By Enrique Toucbda, Albany, N. Y.

(Wilkes-Barre Meeting, September, 1921)

For a number of years prior to the world war, the firm of Geo. H. Thacher & Co., of Albany, N. Y., was engaged in the manufacture of marine and other gray-iron castings. At the outbreak of the war the firm decided to specialize in the manufacture of propeller wheels. It attacked the problem, therefore, from a foundry point of view, seeking to produce a casting that would be so accurate that no subsequent machining would be required on the blades, also from the point of view of the ship builder.

There were two general methods of manufacture, the shortcomings of which have been freely acknowledged. In the sweep method, the nowel, or bottom half-mold, for each blade is swept up by a spindle beam and pitch race, while the top half-mold for each blade is built up individually. In the pattern method one individual blade, with the hub or hub portion, is mounted on a spindle and the individual blade mold formed, the pattern is then rotated on the spindle to the position for the next blade, etc. In rare cases wheels were made from a solid pattern. Owing to the cost of the pattern, its failure in many instances to be correctly made, and (when made of wood) its early and sure distortion the disadvantage of this practice is obvious, while metal patterns in most instances were prohibitive in cost. In these methods both green-sand and loam molding was practiced. The casting produced by either method can be considered only as a blank from which the propeller must be machined. The back surface of each blade must be chipped to the templet and through this procedure chipped to such accuracy as will be required for a static balance. Inasmuch as the work done by the machine tool is confined to the driving face of the blades, not only is perfection most difficult, but corrosion will be greater because of the removal of the dense skin of the casting and the local strains set up by the pneumatic tool in chipping.

To produce a finished 9-ft. propeller for a Navy destroyer required from 8 to 21 days of foundry work and about the same length of time for the machining. Through the use of the Thacher process, only as many hours are required, besides it is possible to produce a finished casting in perfect conformity with any particular propeller-wheel design.

The method is fool-proof against inaccuracy for each part of the mold is contained within and supported by a cast-iron casing, or container, the dowel pins of which are fashioned to engage accurately the holes in the casing or bedplate to which it is to be attached. So accurately made are the various parts of the cast-iron flask that, in the case of flask and mold equipments covering certain limiting diameters and pitches of wheel, any part of one outfit is interchangeable with the same part of any other similar outfit. A perfect propeller wheel was cast in a foundry just outside of Boston from a completely assembled mold made up in Albany that was shipped, uncrated, by ordinary freight.

Equipment for Molding Propeller Wheels

The equipment necessary for the molding of a propeller wheel consists of: (1) base or assembly plate, (2) templet or jig, (3) nowel pattern plate,

Fig. 1.—Base, or assembly plate, with nowel and cope.

(4) cope container, (5) nowel pattern block, (6) cope pattern block and blade pattern 6-*A*, (7) nowels or drags (one for each blade), (8) copes, (9) center plate, (10) center arbor, (11) arbor cap, (12) pouring ring or basin.

The base plate, nowel plate, cope container, nowels, and copes are built sufficiently heavy to eliminate spring or twist. The base plate is permanently located on the foundry pouring floor. The nowel plate,

container, copes, and nowels have suitable adjustable trunnions for rolling over in the molding operation. The copes and nowels are made with adjustable sand-carrying bars to accommodate variations in pitch requirements and are adjustable to either right-hand or left-hand wheels. The pattern blocks are built to standard pitch and are usable for wheels of the same pitch with varying diameter within the equipment capacity by simply changing the blade form *6-A* on the cope pitch block *6*.

Base or Assembly Plate

For small wheels, this is a round iron casting, the top surface of which has been machined to a true plane; in the largest sizes, it is made in two or three parts. A hole is drilled in the center by means of which the jig used when drilling the holes for the flask assembly is located. This base is shown in Fig. 1.

Jig, or Templet

The jig is built from a drawing and is machined and drilled to the finest possible exactitude. It is used as a master jig particularly for locating holes in the base plate, nowel pattern plate, cope container, nowels, and copes. It is made of cast iron and is machine finished to a true surface. It is drilled for attaching to the nowel pattern with locating holes from the jig for positioning the nowels.

FIG. 2.—COPE CONTAINER AND COPE PATTERN BLOCK AND BLADE PATTERN.

Cope Container

The cope container *4*, Fig. 2, is built up of cast iron preferably on a machine-finished cast-iron plate with two sides and the blade end set on the draft angle. The hub end may be set at an angle of 90°, for a four-blade wheel, or 120° for a three-blade wheel. These ends and sides are

bolted, through machine-finished flanges, and the top flanges are planed to a true surface parallel to the bottom-bolted plate (which has been previously drilled for attaching the pattern). Locating holes are drilled in the top flanges from the jig for positioning the copes. The inside area of the container is equal to the area of the nowel pattern block and cope pattern block, before separating.

Nowel Pattern Block

The nowel pattern block *5*, Fig. 3, is built of suitable pattern wood on a machine-finished plate with spindle, arm, and race for generating the desired pitch. The nowel pattern, at the base, is the same shape as the

FIG. 3.—NOWEL PATTERN PLATE AND NOWEL PATTERN BLOCK.

large end of the container with drafted sides and tip end is on the angle for draft. Usually the taper is 1 in. per foot height. The hub end is at an angle of 90 or 120° at the center line. After the block is built of the desired dimensions, a top deck of mahogany, cherry, or other suitable wood is put on and swept down to the true pitch designed and the cope pattern block is built thereon.

Cope Pattern Block

The cope pattern block *6*, Fig. 2, is practically similar to the nowel pattern block, as it is built immediately thereon with its contacting surface matched to the true pitch deck of the nowel pattern block. This block construction is then carried on until the two nowel and cope blocks represent the inside area, shape, etc. of the container *4*. The nowel and cope blocks are separated on the pitch plane so that each block has an accurate true pitch plane surface. A portion of the hub and fillet is

attached to the nowel block *5* and a portion of the hub, fillet, and complete blade pattern *6–A* is attached to cope block *6*. The nowel pattern block *5* is then ready for attaching to the nowel-pattern plate *3* and the cope-pattern block *6* is ready to be dropped into the cope container *4* and attached to the bottom plate.

Nowels, or Drags

The nowels, or drags, *7*, Fig. 1, are made of cast iron. They are rectangular except for one open end, which is angular (as in container and nowel plate). They are open at the top, to set over the pattern, with cross bars at the bottom for sand carrying and strength. The top and bottom have heavy flanges, which are machine finished in parallel planes; the locating holes are positioned therein from a jig.

FIG. 4.—NOWEL, OR DRAG; ALSO CENTER PLATE, CENTER ARBOR, AND ARBOR CAP

Copes

The copes *8*, Fig. 1, are built of cast iron. Their general construction is similar to that of the nowels. They have heavy ribs spaced at suitable intervals and the top and bottom flanges are machine finished in parallel planes. The holes are located from a jig.

Center Plate

The center plate *9*, Fig. 4, is a small cast-iron circular plate, machine finished over its entire surface, with a boss at the center of the under side

for positioning on the main assembly plate *1* and a center hole in the boss for the insertion of the center arbor *10*. On the upper side of the plate *9* are projections for attaching the core sand.

Center Arbor

A hollow iron casting with two turned end bearings for carrying center core forms the center arbor *10*, Figs. 1 and 4. It is set into the center plate *9* and is centered at the top in the arbor cap *11*, Fig. 4.

Arbor Cap

A cast-iron ring with the center attached by brackets at the top forms the arbor cap *11*, Fig. 4. It is dropped over the center arbor *10* and on to

FIG. 5.—MOLD WITH POURING RING IN CENTER.

dowels for positioning on the copes *8*. It is made up with sand to carry a head of metal on a riser on the hub of the wheel.

Pouring Ring, or Basin

The pouring ring *12*, Fig. 5, is a circular cast-iron trough into which metal is poured, in order that it can flow through the gates to each blade mold. The metal flows through each blade, unites in the hub, and rises up through the hub riser until sufficient head is established to provide solidity.

Description of Molding Operations

After the base or assembly plate *1* has been placed on the foundry pouring floor, the nowel pattern plate *3* with the pattern block *5* is set on a substantial floor, and nowel *7* is placed over the pattern on the plate and is bolted to the plate through templet holes in both. It should be remembered that the face of the pattern plate and both top and bottom flanges are accurately machine finished, in parallel planes, so that with the nowel in position and bolted to the pattern plate, the bearing flange face of the nowel is in perfect contact with the pattern plate. It is not possible to enter the finest gage between the contacting surfaces. The pitch plane on the pattern is therefore definitely positioned inside of the nowel, with relation to the contacting surfaces and the drilling therein.

A suitable, strong, dry, sand facing is riddled on to cover the pattern block. A weaker dry sand mixture is then evenly rammed or tamped, as the sand is dropped in, until the nowel is full and butted off even with the cross ribs and flanges. A machine-finished dry plate is bolted on to the nowel bottom and the nowel and nowel plate are rolled over and deposited on a core-oven truck. The nowel pattern plate is then unbolted and drawn off, using guide pins. The nowel is then ready for baking. The nowel plate is replaced on the floor and the second nowel is placed in position and bolted thereon. It will be observed that the pitch plane of the pattern by this procedure has been transferred from the drilled and planed surface of the pattern plate to a similar fixed location with relation to the planed nowel flange surfaces.

The same operation is conducted in the molding of the copes. While the description indicates that the copes are molded after the nowels, the two operations would naturally proceed at the same time. In the case of a 9-ft. three-blade, destroyer wheel, or similar wheels up to 12 ft. in diameter, with both cope and nowel production as described, the average molding time would not exceed 5 to 6 hr. The mold is baked for from 16 to 18 hr. in an ordinary core oven at temperatures from 360° to 420° F. (182° to 216° C.), after which it is ready for assembling.

Assembling

The assembly plate is thoroughly cleaned and each successive baked nowel is placed and bolted in position, as fixed by the jig. The baked copes are successively placed on the nowels and similarly bolted, the center plate *9* being lowered in place in the center hole of the assembly plate and the joints between the copes and the nowels are closed through the top opening by the use of slurry or lead paste. The center arbor *10* is entered into the center plate *9*, the arbor cap *11* is set over the center arbor *10*, and the pouring ring *12* is set on the copes and made up; the mold is then ready to pour. The operation of assembling the mold requires about 3 hours.

The finished wheel must be perfect in diameter, location of center core, uniformity of pitch, correct blade location, and uniform blade thickness. In short, a perfect propeller wheel should result because the base plate is correctly machined; the positioning holes are located by templets from the center at the correct angle and distance; also, the pitch plane in both the nowel and the cope patterns is transferred from the machine-finished surfaces of the nowel pattern plate and the cope container to the fixed position from the machine-finished surfaces of each cope and each nowel. Therefore, when the machine-finished surfaces of the cope and nowel are bolted together, the two pitch planes of each return to contact, leaving an exact blade thickness, or pattern reproduction, in

FIG. 6.—FOUR-BLADE SEMISTEEL BLADE JUST OUT OF MOLD, WITH TWO BLADES CLEANED OF ADHERING SAND.

each blade mold; and as the top flange in the nowel is machined parallel to the bottom flange of the nowel and all the nowels are of even height, when the nowels are bolted on the machine-finished assembly plate the pitch planes are parallel with regard to the assembly plate and therefore in relation to each other.

Fig. 6 shows a four-blade semi-steel propeller wheel just out of the mold, with two blades cleaned from the adhering sand. After chipping off the fins at the blade edges, removing the sprue, and boring the hub, the wheel is ready for shipment. Besides, the wheel as cast will be much more perfect and in much better balance than a machined wheel cast by the ordinary methods.

The same practice applies to the molding of individual blades, with the same economy of time, material, and accuracy of production.

It should be made plain that the process is adaptable for molding-machine use, which further lessens production cost. Wheels having blades of substantial size have been completely molded on a combination jolt and roll-over machine. While to date a roll-over device large enough to handle a 20-ft. wheel has not been made, the construction of such a machine is in contemplation.

The mold is poured through gates to each blade, insuring uniformity of flow and metal distribution, as well as casting solidity and clean metal The casting is left in the mold about 24 hr. to avoid any danger of internal strains. The equipment is ready for the production of the next wheel as soon as the sand is shaken out of the cope and nowel. This sand, when cooled and wet down, can be used again on top of a new facing of sufficient depth to cover properly the pattern blocks.

Standardization of Equipment

For wheels built integral and for commercial use, the equipment is built in three standard sizes, 12 ft., 16 ft., and 20 ft. in diameter. Each unit is designed for either three- or four-blade wheels. For built-up wheels, the same standards are maintained.

Pattern-block Standardization

The patterns are standardized in diameter to suit the equipment diameter capacity, and in pitch to standard practice. For example, the patterns for the 16-ft. equipment would be of sufficient length to fit the container and consequently of diameter capacity from 12 to 16 ft. The pitches on the pattern blocks are standardized for, say, 6 in. pitch variation and the required pattern blocks for the 16-ft. equipment would be 14 ft. 0 in., 14 ft. 6 in., 15 ft. 0 in., 15 ft. 6 in., 16 ft. 0 in., 16 ft. 6 in., 17 ft. 0 in., 17 ft. 6 in., and 18 ft. pitch; or nine pitch blocks only are required to manufacture wheels of any diameter from 12 to 16 ft. and with any combination of standardized pitch.

Assuming that wheel diameters increase by 3-in. variations, 108 combinations of wheel diameter and pitch may be made from nine standard pitch blocks by simply changing the blade form and area on the pitch block. Thus, while the initial cost of one pattern block, including blade form, may exceed the cost of the ordinary blade and hub portion, the total pattern cost, by the use of this process, is ultimately greatly reduced.

Tests to Determine Fidelity of Casting to Pattern Design

Fig. 7 shows a wheel mounted on a balancing stand by means of a balanced turned arbor, in which are placed suitable keyways. Keys are inserted on each side of the hub. Through such a test, not only can the

static balance of the wheel be determined, but by bringing a templet into contact with similar sections of each blade it will be seen that the wheel is uniform and correct in diameter, pitch, blade-thickness, and balance from an established center, which through this procedure is accurately located for the subsequent boring that is necessary to fit the wheel to the end of the propeller shaft.

Many tests have been conducted to prove the accuracy and delicacy of this test. In one case three propellers cast from the same pattern

FIG. 7.—WHEEL MOUNTED ON BALANCING STAND.

and the hubs machined exactly alike, when tested were found to weigh 10,430, 10,435, and 10,440 lb. Four single blades cast from the same pattern, after the blade seats were machined, weighed 3675, 3675, 3675, and 3670 lb.

Fig. 8 shows an 18 ft. 6 in, four-blade, 18-ft. pitch, built-up wheel being installed on the steamer "Mystic." The weights of the four blades on this wheel were 3475, 3475, 3475, and 3470 lb. In operation the slip was reduced from 16 to 9 per cent. and the time saved in the round trip voyage was approximately 10 per cent.

The steamer "Patrick Henry," a standard U. S. Shipping Board vessel, of 12,500 deadweight tons, which was equipped with a Thacher process propeller, made on a light load trial trip a speed of 12 knots, which means a substantial gain over identical type ships having other makes of propellers. The weights of the four blades were 4345, 4345, 4348, and 4350 lb.

In Fig. 9 is shown a three-blade built-up manganese-bronze propeller made by the Thacher process. This wheel when tested on a balancing

FIG. 8.—FOUR-BLADE, 18-FT. PITCH, BUILT-UP WHEEL OF STEAMER "MYSTIC."

stand developed no variation in balance. It is one wheel of a twin-screw installation on the steamer "Herman Frasche."

METAL USED IN PROPELLERS

In propellers used in the Navy, manganese bronze, having an ultimate strength of 70,000 to 80,000 lb. per sq. in. and an elongation of 20 to 35 per cent. is specified.

For commercial use many wheels have been made of semi steel. In the case of thirty such wheels, the lowest ultimate strength was 32,555 lb.

per sq. in., the highest 42,175 lb. per sq. in.; while the average was 36,658 lb. The breaking of propeller blades has not been uncommon; in most cases this has been attributed to lack of perfect balance. It is not unusual for an 18-ft. wheel to have a tip speed of over 5500 ft. per min.

By the use of this method, the following features can be guaranteed: The diameter will be a true circle; blade angle will be accurately estab-

FIG. 9.—THREE-BLADE, BUILT-UP, MANGANESE-BRONZE PROPELLER.

lished; pitch will be absolutely uniform; blade thickness will be correct to design; balance will be true in any position of wheel; more prompt delivery can be assured. From the foregoing there must result greater speed for same power, lower repair cost, fewer replacements, and more ship-service days.

The Electric Furnace in the Iron Foundry

By Richard Moldenke, E. M., Ph. D., Watchung, N. J.

(New York Meeting, February, 1921)

One of the gravest problems of the iron foundry today is the accumulation of sulfur in commercial scrap and its effect on the castings made therewith. The ordinary jobbing castings today show a sulfur content of 0.18 per cent., and occasionally as high as 0.22 per cent. The product of the foundry during the war is undoubtedly to blame for this rapid increase and conditions will become worse as the millions of tons of gray-iron castings of the war period return to the foundry in the form of commercial scrap.

In the ordinary cupola remelting of pig and scrap, at least 0.02 per cent. sulfur is taken up; often double that amount. The high cost and difficulty of obtaining pig iron during the war period compelled the use of considerable scrap in the mixtures; frequently charges containing 90 per cent. of bought scrap were melted. Naturally the sulfur content of the castings increased.

Until the advent of the basic-hearth electric furnace, the only method of holding the sulfur within reasonable limits was to use high percentages of pig in the foundry mixtures. Pig iron seldom contains over 0.05 per cent. sulfur, if well made. With pig iron forming 60 per cent. of the charge and the gates, runners, rejections, and bought scrap the other 40 per cent., the sulfur content of the castings can easily be held down to 0.10 per cent. Pig iron, however, costs more than scrap even when melting loss differences are considered, hence as small a percentage as possible will be used.

The recent advance in knowledge of rational melting and the consequent reduction in losses directly due to oxidation of the metal and cold iron, has permitted the acceptance of castings with a much higher sulfur content than formerly. The steel industry also is seeking to determine how high sulfur may go with safety. In the iron foundry, however, there is the danger of a low cupola bed or an unduly retarded air-furnace heat, with the consequent raising of the freezing point of the metal and segregation effects resulting from high sulfur with insufficient manganese. The iron foundryman must, therefore, have a means of correcting his

molten metal. The electric furnace, with a basic hearth, offers this opportunity.

Before the iron foundryman, particularly the producer of gray and malleable iron castings, can pour his molds safely, the molten metal must have a high degree of superheat, be thoroughly deoxidized, and reasonably low in sulfur. A foundryman will get these characteristics if he uses good materials and melts properly. The electric furnace will give a highly superheated metal that is thoroughly deoxidized, and a fine degree of desulfurization if the hearth is basic. If, for greater economy and to fit existing equipment conditions, the "duplexing" system—cupola metal refined in the electric furnace—is used, the best results for quality are obtainable conjointly with a reasonable cost.

The foundryman may melt cold metal directly in the acid or basic-hearth electric furnace, or he may refine molten cupola or furnace metal in either hearth electric furnace. In duplexing, however, it is doubtful if open-hearth metal will be transferred to the electric furnace; in fact it is doubtful if even air-furnace iron will be used that way, as in the foundry the air furnace gives 10 to 40 tons of metal at one time, whereas the same tonnage from the cupola is either distributed over 2 to 4 hr., or spread over the entire working day. The problem of the electric furnace in the foundry, therefore, resolves itself into either adding the necessary electric equipment for duplexing, or installing electric furnaces for direct melting and refining of cold stock. Of the two hearth systems the basic is to be preferred for its specific value in desulfurization.

Cost of Melting Cold Metal in Electric Furnace

When cold metal is charged into an electric furnace, unless carefully handled, there will be considerable fluctuations in the current until the pigs or pieces of scrap around the electrodes are melted. As the rest of the charge melts in the bath that forms, the fluctuations become less marked and when the bath is entirely molten the internal resistance is sufficient to reduce the current demand, in some furnaces, one half. Melting cold iron ordinarily requires a big current reserve and a higher current cost. Data from steel melting show that melting cold stock consumes up to four-fifths of the total current used, the refining period takes the other fifth. Since, however, refining is going on while melting progresses, the contrast in reality, is not so great. Duplexing is not only cheaper but it is also faster, for melting a cold charge and refining it in the electric furnace might take 2 hr., whereas the refining period after melting would not reach ¾ hour.

The advantage of the melting-from-cold-metal system over duplexing lies in the ability to melt whenever desirable, whereas duplexing is dependent on the running time of the cupola. The higher cost of cast-

ings by either method, unless the lower grade materials used make up this difference, means that the electric furnace will only be used where quality work is produced. Thus, if the total cost of work is, say, 3c. a lb., it is not likely that the foundryman will add another ½c. to ¾c.; but for work that costs 15c. a lb., this addition matters little. The maker of grate bars will undoubtedly stick to the cupola, whereas the producer of piston rings is already beginning to use the electric furnace.

Influence of Electric Furnace on Foundry Methods

A foundry melting metal all day is the exception. The general custom is to keep the men molding until blast is put on and melting begins, which is usually so timed that the heat will be completed as near quitting time as possible. When the first iron comes over the spout, the men stop work and prepare to pour off their molds. In the malleable industry, particularly with furnace iron or where the nature of the castings lends itself to the purpose, melting goes on all day, as in a large cast-iron carwheel shop, and molders mold continuously while a special gang pours. This is the ideal way of conducting operations.

Electric furnaces of large tonnage are expensive, a 3-ton outfit, which ordinarily would be considered quite large, costs about $35,000 at this writing. For a moderate degree of refining—that is superheating, deoxidation and desulfurization—the metal, as taken from the cupola, should remain in the electric furnace at least ½ hr. With rapid repairs after tapping out, fully ¾ hr. will be required for each batch of molten metal. For an average foundry, melting say 20 tons daily in a 54-in. cupola, the heat will last 2 hr., which permits the treatment of only half of it by the duplex method. Unless the product of the establishment can be divided into high-grade and ordinary work, the duplex process will be difficult to install with the present daily routine. Foundries can do this in most cases, hence an electric-furnace equipment added to the ordinary foundry will work out very nicely.

Where it is necessary that one casting will be as good as the next, the entire heat must be melted from cold stock or duplexed. As by using high sulfur pig irons, large percentages of low-grade scrap, briquettes of borings, punchings, shot, etc. it is possible to get from the electric furnace, when melting cold stock, as cheap a molten metal, fully refined, as from the cupola, duplexing will not be required, and electric-furnace heats may be taken off all day long if desired. But unless a shop is run on the all-day pouring plan, the owners will hardly care to make the necessary changes in methods such a radical operating departure produces, unless accompanied by a complete shutdown during the transition period.

Advantages of Basic-hearth Electric Furnace

The selection of the basic-hearth electric furnace involves several considerations. In the acid-hearth furnace, the slag situation is easier, deoxidation is readily accomplished by providing a slag cover with additional periodic charging of fine coke on this to hold the furnace atmosphere neutral. The intense heat of the bath, with its high carbon percentage, takes care of all oxygen that may be in the metal in some combination. The disadvantages of the acid-hearth furnace are that, whether melting cold metal or duplexing, it is necessary to start with comparatively good material, as the sulfur problem remains. Further, there is a marked addition of silicon in the bath by reduction from the silica hearth and slag, if refining is carried on for any length of time. The advantages of the acid-hearth are the cheaper refractories required, the furnace body lasting as long as an open-hearth furnace, and in much easier slagging conditions. Where, therefore, the question of extremely low costs is not so serious an item, there is no reason why an acid-hearth electric furnace should not be used for melting from cold metal, for the sulfur can be held down by using high percentages of good low-sulfur pig iron—the melting process gives no additional sulfur, as is the case in cupola melting.

In view, however, of the sulfur conditions in purchased scrap and the desirability of holding down the sulfur maximum, the basic-hearth electric furnace should be used in every new installation, whether for cold melting or duplexing. Nothing prevents running an all-scrap heat through the cupola for ultimate refining in the basic-hearth electric furnace. The carbon conditions can be regulated in the cupola sufficiently, or if necessary in the electric furnace by steel scrap additions, if time can be given for this purpose. The silicon can be increased, if desired, by adding ferrosilicon, and such elements as nickel, chromium, titanium, etc., provided by direct or ferroalloy addition, or preferably and far cheaper in the pig iron originally used.

Control of Phosphorus and Manganese in Castings

As the electric furnace for the foundry is intended to improve the molten metal only in regard to initial heat, freedom from oxygen in some combination, and elimination of sulfur to the desired minimum, the question of a possible phosphorus reduction does not come up. In fact, unless the steel stage is passed through this is out of the question anyhow. The iron foundry deals with three ranges in phosphorus. In the malleable casting the phosphorus must range from practically nothing to a maximum of 0.200 per cent. For gray iron the low range is anything under 0.300 per cent.; actually it will be around 0.175 per cent.

and results from using bessemer pig irons or the "malleables" in the mixture. Heavy castings should not go above the 0.300 per cent. limit, also the lighter sectioned work of large dimensions, particularly when ribbed—as in condensers for marine purposes. Ordinary castings have about 0.500 per cent. phosphorus, this range being from 0.300 to 0.700 per cent. The high range is anything above 0.700 per cent. and is confined to light castings of an ornamental nature, such as stoves and radiators. Foundrymen have no difficulty with their phosphorus, as it can be regulated by suitable purchasing of pig and scrap, steel scrap being free from phosphorus and stove-plate scrap full of it.

Whenever the product of a foundry runs below 0.50 per cent. manganese, there must have been defects in the melting practice, involving undue oxidation during the operation, unless the mixture was too low in manganese in the first place. Where, with sufficient manganese in the mixture, the castings come out below 0.50 per cent. either burnt scrap has been used or the bed of the cupola was too low and free oxygen from the blast attacked the melting iron. The manganese percentage in such a case was insufficient to care effectively for the surplus oxygen and by uniting with it enter the slag; hence oxidized metal with pinholes, excessive shrinkages, cracks, etc. was produced. With high sulfur in addition, none of this can be neutralized by available manganese, hence further trouble. With thorough deoxidation and desulfurization effected in the basic-hearth electric furnace it is possible to start with lower manganese ranges in the mixtures;[1] indeed, it is necessary to start with lower manganese, otherwise that part of it in the mixture intended to care for excessive sulfur, were the castings made directly from the cupola, will on desulfurization in the electric furnace remain behind and act as a hardening agent. One well known Southern pig iron is so low in manganese that foundrymen fear to use it; yet, if properly melted, this iron yields excellent castings.

The metallurgical aspects of the basic-hearth electric furnace operation are interesting: To desulfurize rapidly and well, it is necessary to keep the lining in good shape and to charge lime with a little fluorspar to form an active slag on the molten metal. Crushed coke is also charged on the slag in order that the interior atmosphere may be kept neutral to reducing. The more active the lime the quicker is the reduction in sulfur. Calcium carbide is formed and the bath is both deoxidized and desulfurized. A shallow bath is quicker than a deep one, for the greater the slag and metal contact area the better is the interaction. While it is possible to get the sulfur content as low as 0.009 per cent.,[2] this reduction is not necessary in ordinary practice. Reductions to 0.04 or 00.5

[1] Geo. K. Elliott: *Trans.* Amer. Foundrymen's Assn. (1920).

[2] Geo. K. Elliott, a pioneer in duplexing cast iron; also by W. G. Kranz, of "triplex" malleable fame.

per cent. are quite sufficient, for to go lower requires a rapidly increasingly proportional current and time consumption.

Cost of Melting in Electric Furnace

The matter of costs is a wide subject, for much depends on the furnace used. In the figures here given a fairly high average has been assumed. The chief item—cost of current—varies in localities. The present general rate is about 1.5c. per kw.-hr., hence this has been used in the calculations. On a 3-ton basis, melting cold stock would require roughly 530 kw.-hr. per ton. In duplexing it is possible to get along with 100 kw.-hr. This would mean a current charge of $7.95 and $1.50, respectively. To the latter figure, however, there should be added the cupola melting cost, for purposes of comparison. At present this costs at least $4 a ton; in normal times one-half of this would be considered high.

The cost of electrodes varies somewhat with the type of furnace. Where the construction allows air currents to enter the furnace body and pass out around the electrodes there is bound to be a heavy carbon consumption. So allowing 20 lb. of electrode per ton for melting from cold stock (or at 8c. a lb., $1.60 a ton) and 60c. a ton for duplexing, this item would be covered. Refractories for repair purposes, including the periodic complete rebuilding of the furnace body, amount to 45c. a ton for an acid-hearth electric furnace, and about $1.50 a ton for the basic system.

Labor for the melting from cold stock costs about $2.50 a ton, while with duplexing the cost is about $1.50—the labor of charging the raw materials going to the account of cupola melting. The subject of depreciation, interest, etc., when figured on the basis of 300 heats annually—or corresponding to duplexing conditions, will run about $2 a ton, on a 20 per cent. basis on the investment. With continuous running, whether electric melting only or duplexing, and a consequent possibility of many more heats annually, this charge will be lowered materially.

Summarizing these costs per net ton gives the following:

	Cold-metal Melting Acid Hearth	Duplexing Basic Hearth
Current	$7.95	$1.50
Electrodes	1.60	0.60
Refractories	0.45	1.50
Labor	2.50	1.50
Depreciation, etc.	2.00	2.00
	$14.50	$7.10
Adding cupola melting cost		4.00
		$11.10

If all the metal of a foundry were duplexed, it would be possible to effect a saving, in each of the above cases, of practically the whole amount through the use of briquetted borings, steel, malleable, stove plate, and other scrap—to the exclusion of practically all pig iron—whether these are melted in the electric furnace or run through the cupola. In pre-war times when the ordinary cupola mixture might have cost $15 a ton, certain sash-weight foundries were putting mixtures costing only $6.50 through the cupola. Even in these days, metal equal to charcoal iron is produced, in the basic-hearth electric furnace, from burnt soda kettles, burnt stove grates, spring beds, old annealing pots, etc. On the other hand, where only part of a cupola heat is to be duplexed, or where time is not available for an extended refining treatment in the case of electric melting from cold stock, the regular run of cupola mixtures must be used to insure the desired results. If all foundrymen were to use the undesirable lines of scrap on the market, these would soon be sold on their metallic iron content and compete directly with pig iron. With a good metallurgical laboratory, a foundry could accomplish much in the way of cost reduction where a basic-hearth electric furnace is available.

The interesting point to be noted from the costs given is that for an ordinary foundry prepared to duplex some or all of its cupola metal, the additional cost is but ⅛c. per lb. Because of compensations in the form of lighter runners and gates, due to the intense heat and wonderful fluidity of electrically refined cast iron and as the number of castings misrun is much smaller than the present practice with cupola or furnace, and as the quality of the work is unquestionably higher, this third of a cent becomes at least a part of a cent received.

Those who have observed the tapping out of an electric furnace heat of cast iron will have noticed the extreme temperatures of the material. The metal is snow white, and when poured into the molds remains liquid for a long time. The basins draw down funnel-shaped eventually showing excellent feeding qualities on the part of the molten metal; and the castings are close-grained and apparently sound. Hence this kind of iron may be used for high-pressure valves and fittings and other important construction work. The molds must be made of unusually refractory sand and the partings should be clamped very tightly. The fluidity and length of time before solidification takes place make possible the cutting out of many risers and heads, and a reduction in volume of those necessary. This, with the smaller runner sections and the ability to flow long distances before showing signs of cold shuts, should make the subject an attractive one for those foundrymen who would be benefited by such valuable characteristics.

DISCUSSION

GEORGE K. ELLIOTT,* Cincinnati, Ohio (written discussion).—Four years of experience with the electric furnace for treating cast iron, both gray and white (for malleable), has shown that there are at least three general classes of iron castings for which this furnace is an economical feasibility:

1. Those castings in which unusual physical properties (such as tenacity, solidity, and fineness of grain) are desired above all else. In the extreme engineering projects of all kinds that are common today there is a tendency to pass up the homely old-fashioned gray-iron casting for the supposedly more trustworthy malleable or steel. Doubtless often the change is justifiable from every important angle, but in more than a few cases cast iron is rejected solely through ignorance of what really good cast iron is capable of being or through a well-grounded fear that such iron is beyond the reach of the average foundry. When measured by the standards of modern engineering requirements, cast iron is frequently found wanting. This is not so much because of its own weaknesses as the shortcomings of the ordinary foundry processes and the lack of a universal skill and knowledge among foundry operatives. The electric furnace has not so much endowed cast iron with new properties as to show its real properties. For instance, cast-iron valves made from electric-furnace iron have been exposed to superheated steam for several years but not one failure has been reported.

2. Castings that, on account of thinness of section, are ordinarily run only with excessive losses through "cold shuts" and various other manifestations of iron lacking in fluidity. In the electric furnace, any grade of iron can invariably be made very fluid because it can be superheated to any temperature. The cupola is able to do little superheating, consequently certain grades of iron, lacking fluidity but possessing unusual strength, cannot be melted and delivered to the molds hot enough to run out a profitable number of the castings.

3. Castings that are extremely hazardous to the foundryman or to the machine shop from the profit-and-loss point of view. Many castings, for instance cylinders or valves, cannot be tested and therefore are not found to be defective until after considerable expensive machining has been done. In such cases there is lost not only the foundry labor and material but also machine-shop labor and time. By making possible the use of the best kind of iron, by superheating it properly, and by presenting a melt that is entirely free from entrained slag and dissolved gases, the electric furnace brings about a great reduction in shop defectives, and all additional cost due to the process is unnoticed in the general gain.

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* Chief Metallurgical Engineer, The Lunkenheimer Co.

The three classes of castings outlined show advantages accruing to the finished product. There is also the advantage of having low-grade materials made suitable to and accessible for high-grade products. Off-grade pig iron and high percentages of scrap in the mixture can be made into high-class castings through the medium of the electric furnace with basic lining. The foundry some distance from the blast furnaces, with the basic electric furnace, can make available low-grade neighborhood scrap. On the other hand, the foundry close to the blast furnace can buy its iron in the molten condition and by superheating, and refining to any required analysis in its electric furnace, can make it suitable for any desired grade of castings.

W. N. CRAFTS, Montreal, Que.—The electric furnace has suffered from its friends a great deal. You cannot get something for nothing and the electric furnace is not going to take cheap scrap, 100 per cent. borings, or any other poor material and make perfect castings without the addition of considerable technical attention and a large amount of electric current.

A malleable casting must be annealed but a gray-iron casting ordinarily does not. An iron or gray-iron casting made in the electric furnace is subject to metallurgical conditions that I think Doctor Moldenke has overlooked. The refining in the basic electric furnace must be done under a reducing slag in order to get out the sulfur; that means that the temperature must go at least 200° above the normal temperature of the slag in the cupola or the oxidizing slag in the electric furnace or in the open hearth. That, of necessity, means that the metal is going to be hotter than it should be for good pouring. The danger is that the power of the electric furnace is not rated sufficiently high so that the melter will pour his castings at a temperature that will give hardened castings absolutely free from blowholes and of high tensile strength, but an exceedingly brittle iron.

RICHARD MOLDENKE, Watchung, N. J—The point is well taken, but there seems only one thing to do with such highly superheated iron, and that is to let it stand until cool enough to pour. The addition of some cold sprues will quickly cut down the injurious superheat, so that the molds will not be damaged. I have seen such highly superheated iron poured without any trouble, though the foundry had at first found it necessary to get better sand and to clamp the flasks tighter. On the whole, however, this excessive superheat is a good thing as it gives an exceedingly clean metal, every particle of slag rising to the top.

A. L. STILLMAN, New York, N. Y.—There is a suspicion that the cast-iron boring briquette is not sufficiently strong to stand the wear and tear of the cupola and that, somewhere, on the way down, it spreads apart.

Practice has shown that the briquette does actually melt all the way through. I was present at a test, not long ago, where certain briquettes were poured on with the idea of running the thing with as much consideration for the briquetted borings as possible. The pig was put on first, then the heavy scrap, followed with the 10 per-cent. briquettes, and after that the coke. But instead of throwing the coke on the briquettes, the laborers threw a load of pig iron into the cupola, but the cast-iron briquettes stood under that.

So I think that unless the dye industry is prepared to absorb all the cast-iron borings, that this method will be universally adopted.

The limit of the briquetting at present is 20 per cent., but we can hope for at least 40 per cent., if necessary in duplexing methods, if the borings are available on account of the refinement and the greater flow that will be obtained. Above 20 per cent. in the cupola, the addition of briquetted borings must greatly increase the sulfur content and the formation of hard iron.

G. F. Cone, New York, N. Y.—Does the electric furnace make alloy castings possible some time in the future? Is there likely to be a demand for castings of this kind?

Richard Moldenke.—Gray cast iron is fundamentally a steel of given combined carbon content plus mechanically mixed graphite. Any improvement by adding such metals as nickel, chromium, etc., would be attained by putting these metals into the steel structure and leaving the graphite the same. My opinion is that such metals should enter the iron by way of the blast furnace rather than in the shape of ferroalloys. It is much cheaper.

I am just finishing a series of tests for the Bethlehem Steel Co. along this line, with their Mayari pig iron (a nickel-chromium iron) the two metals being in the ore as charged into the blast furnace. The results of these tests will be published shortly, and will doubtless prove of great interest.

It will be difficult to produce gray iron castings economically enough when ferroalloys are used—except for special purposes. Hence more attention should be devoted to the use of suitable ores of the metals wanted in the pig iron to add to the regular stock.

H. A. Schwartz, Cleveland, Ohio (written discussion).—Perhaps the largest use of electric furnaces in the iron foundry is in the Kranz "triplex" process for making malleable castings. The experience gained in that process should be applicable to the manufacture of gray iron. It has shown that where costs must be considered the electric furnaces must work on hot-metal charges, must run continuous, and must be of fair

size. In other words, the electric furnace is suited only to plants producing large tonnages of quality metal under conditions, as to crane service, etc., that are prohibitive in the small plant. Only where the desired quality is otherwise inattainable could gray iron made in occasional small heats in the electric compete with a cupola plant.

The fact that the properties of all cast irons are fixed by the form and amount of carbon present was pointed out some years ago by Doctor Howe, yet the carbon content is disregarded by many authors. The total carbon content of cupola metal is limited to a rather close range, from perhaps 2.75 per cent. to perhaps 3.25 per cent. The value, except in the presence of a very badly oxidized melting stock, depends mainly on the cupola melting condition and but little on the melting stock. In the past, this has perhaps been fortunate as it kept the foundryman out of trouble due to variations in total carbon. But it has been unfortunate from the point of view that it made for hazy thinking and spread abroad a disregard for that most important element. There is no reason why 3 per cent. carbon should be an optimum for all purposes and the makers of air-furnace gray iron are able to produce a considerably improved product by attaining a lower carbon content.

The other elements present in iron, except phosphorus, are useful or harmful mainly as they affect the conversion of cementite into free carbon. The electric furnace permits, either by triplexing or by the use of steel punchings, a satisfactory control of the carbon content coupled with a control of the other elements (silicon, manganese and sulfur) that are of importance in fixing its distribution between the free and combined forms. Consequently the field of improving cast iron by electric melting can hardly be said to be limited to the removal of sulfur and oxygen, but rather extends out to include the making of a cast iron of accurately controlled free and combined carbon content.

Doctor Moldenke has rightly emphasized that the reduction of sulfur below 0.04 or 0.05 per cent. is unimportant, given a proper manganese content. The writer would go further and say that there are circumstances where an iron containing 0.009 per cent. sulfur would be improved by adding 0.04 per cent. more of that element.

The work of J. E. Johnson, Jr. on "Oxygen in Cast Iron" should at least create a doubt as to whether that element is always the breeder of harm that many, including Doctor Moldenke, maintain it to be.

The great contribution of electric metallurgy to the gray-iron foundry will come not when it is considered only as a desulfurizer and deoxidizer, permitting the use of "off" pig iron and cheap scrap, important as this may be, but when it becomes a means of quantitative control of the various elements alloyed with iron, in the light of definitely established facts, toward the attainment of the desired physical properties from the viewpoint of carbon control.

As Doctor Moldenke suggests, the burnt scrap and the off heat will soon rise in price if all can and will use them and these trade advantages would disappear. Chemical control, from the viewpoint of quantity and distribution of carbon, would involve improvements similar to those made in the malleable industry in the same way during recent years, and would constitute a permanent metallurgical advance and a consequent benefit to all industries using gray iron.

Manufacture of Ferromanganese in the Electric Furnace*

By Robert M. Keeney,† E. Met., Golden, Colo., and Jay Lonergan,‡ E. M., Wenatchee, Wash.

(New York Meeting, February, 1921)

The electric smelting of manganese ore and the production of ferromanganese did not exist as an industry, in the United States or elsewhere, previous to the outbreak of war in 1914. Ferromanganese had been produced, electrically, during times of high prices by two companies at Niagara Falls and by several European companies, but the production was spasmodic, and none was electrically produced when ferromanganese sold at from $35 to $40 per ton. Thus the electric smelting of manganese ore must be considered as a development caused by the high prices prevailing during the years 1916, 1917 and 1918, and the necessity of smelting domestic ore in order to fill the ferromanganese requirements of the steel industry of the United States, which increased from 189,088 tons in 1914 to 356,356 tons in 1918. The electric furnace is well adapted to smelting domestic ore because it can be located in small units near the source of ore supply. In 1918, the ferromanganese production of the United States was 333,027 tons, of which about 7 per cent., or 23,000 tons, was produced in the electric furnace. The electric furnace not only assisted materially in the development of a domestic-ore supply but made a considerable saving of coke, as it requires about 1¼ tons of bituminous or lignite coal per ton of ferromanganese compared with a blast-furnace consumption of 2.9 tons of coke per ton of ferromanganese.

Some of the plants in the United States that smelted manganese ore in the electric furnace during the war and in 1920 are listed in Table 1. From early in 1919 to about February, 1920, little ferromanganese was produced in the electric furnace. During this period the price of ferromanganese (78 to 82 per cent. manganese) was about $100 per ton. During the first half of 1920, several plants resumed operation when the price of ferromanganese (76 to 80 per cent. grade) gradually increased to $200 per ton, delivered.

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* A contribution from the Department of Metallurgical Research, Colorado School of Mines, Golden, Colo.

† Director of Metallurgical Research, Colorado School of Mines.

‡ Chief Engineer, Royal Development Co.

TABLE 1.—*Electric Ferromanganese Plants in United States*

Company	Location	Capacity, Kv-a.	Number of Furnaces	Size of Furnace, Kv-a.
Anaconda Copper Min. Co.	Great Falls, Mont.	25,000	5	5000
Bilrowe Alloys Co.	Tacoma, Wash.	2,100	6	350
Ferro Alloy Co.	Utah Junction, Colo.	2,700	3	450 750, 1500
Iron Mountain Alloy Co.	Utah Junction, Colo.	3,000	2	1200, 1800
Noble Electric Steel Co.	Heroult, Calif.	4,500	5	800 to 1600
Pacific Electro Metals Co.	Bay Point, Calif.	3,000	1	3000
Pittsburgh Metallurgical Co.	Montour Junction, Pa.	1,500	1	1500
Southern Manganese Corp.	Anniston, Ala.	15,000	8	1500 to 3000
Western Reduction Co.	Portland, Ore.	1,200	2	600
Total		58,000	33	

With present coke prices the electric furnace can probably manufacture ferromanganese as cheaply as the merchant blast furnace, because the fuel cost per ton of metal is about the same as the power cost per ton of metal. During September, the price of ferromanganese dropped to $175 per gross ton delivered, due to overproduction and importations from England; in November, the price was $135 per gross ton delivered.

PROCESS

As in electric smelting of iron ore, the process consists essentially of the substitution of electric heating for combustion heating, with the use of carbon as a reducing agent and limestone or lime as a flux of the silica in the ore. The fundamental reactions are:

$$MnO_2 + 2C = Mn + 2CO$$
$$MnCO_3 + C = Mn + CO_2 + CO$$
$$MnCO_3 + 2C = Mn + 3CO$$
$$Fe_2O_3 + 3C = 2Fe + 3CO$$
$$FeO + C = Fe + CO$$
$$2SiO_2 + 3CaO = 3CaO.2SiO_2$$
$$2SiO_2 + 3CaCO_3 = 3CaO.2SiO_2 + 3CO_2$$

with excess of carbon there is a tendency to form calcium carbide

$$2SiO_2 + 3CaO + 3C = 2CaO.2SiO_2 + CO + CaC_2$$

which results also in loss of manganese in the slag because of lack of lime to combine with the silica.

$$3CaO.3SiO_2 + MnO = MnO.3CaO.3SiO_2$$

Excess lime results in the formation of an air-slacking slag due to the formation of the orthosilicate $2CaO.SiO_2$.

$$SiO_2 + 2CaO = 2CaO.SiO_2$$

The chemical reactions involved are about the same as in blast-furnace smelting, except that, due to the high temperature at the end of an electrode in an electric furnace, there is a tendency to form calcium carbide if excess lime or carbon is present. This is due to poor mixing of the charge so that lime and coal alone are in contact at the end of the electrode. On the general grade of manganese ore smelted during the war, the total loss, slag loss, and stack loss seem to be about the same in both processes. In such a comparison, the electric furnace is at a disadvantage as, from all evidence available, the electric-furnace charges evidently carried less manganese and more silica. With this lower grade ore, the electric furnace accomplished practically the same results as the blast furnace smelting higher grade ore.

Electric Smelting Versus Blast-furnace Smelting

P. H. Royster[1] of the U. S. Bureau of Mines, who studied the operation of eleven ferromanganese blast furnaces, gives the results of forty experimental periods of ten days each, the average of which is shown in Table 2. Similar results have been compiled from three months operation of an 1100-kw. electric furnace. The weights given in Table 2 for the electric furnace are determined by actual weighing and all figures are based on metal cleaned and sorted.

The losses in both furnaces are the same, though the electric furnace was smelting an ore containing 34.8 per cent. Mn and 13.2 per cent. SiO_2 and the blast furnace was smelting ore containing 40.33 per cent. Mn and 8.6 per cent. SiO_2. The electric-furnace slag was less basic than the blast-furnace slag.

The fuel in the blast-furnace charge is the cause of the slag fall from the blast furnace being greater than that from the electric furnace. There is a possibility that the difference in slag fall is caused by the fact that most of the blast-furnace slag was estimated by volume. As is to be expected, the most marked difference in the two processes is in the carbon consumed, the blast furnace requiring 5323 lb. (2414.5 kg.) per

[1] P. H. Royster: Production of Ferromanganese in the Blast Furnace. *Trans.* (1920) **62**, 18.

TABLE 2.—*Electric Furnace versus Blast Furnace*

	Blast Furnace	Electric Furnace
Ore per ton metal, pound	5992.0	6544.0
Coke per ton metal, pound	6326.0	
Coal per ton metal, pound	200.0	2839.0 (lignite)
Limestone per ton metal, pound	2349.0	1063.0
Lime per ton metal, pound		253.0
Ore analyses:		
Mn, per cent	40.33	34.8
SiO_2, per cent	8.60	13.2
Slag, per ton metal, pound	3196.0	2830.0
Metal, per cent. Mn	74.9	73.6
Metal, per cent. Si	1.15	2.9
Slag analysis:		
CaO, per cent. }	41.75	37.8 } 40.2
MgO, per cent. }		2.4 }
Al_2O_3, per cent	14.0	7.9
SiO_2, per cent	28.1	28.6
Mn, per cent	10.6	12.4
Carbon per ton metal, pound	5323.0	1273.0
Mn, charged, pound	2382.0*	2291.0
Mn, per cent. to metal	72.0	72.0
Mn, per cent to slag	14.7	15.0
Mn, per cent. lost in stack	12.8	13.0 (by difference)

* Blast-furnace figures do not check with electric-furnace figures because of method used to obtain them.

NOTE.—Unless otherwise specified, the gross ton of 2240 lb. is used in this paper.

ton of ferromanganese and the electric furnace 1273 lb. (577.4 kg.). On the whole, the metallurgical results obtained by the two methods are the same, except that the electric furnace will apparently smelt an ore containing 5.5 per cent. less manganese and 4.6 per cent. more silica with the same recovery as the blast furnace.

PLANT

The electric furnaces were installed in a wooden frame building with corrugated iron siding and roofing. This construction was rendered necessary by war conditions and caused the furnaces to be placed farther from the transformers than would have been necessary with fireproof construction. The furnace installation consisted of one 1200-kv-a. and one 1800-kv-a. three-phase furnace. A flow sheet of materials is shown in Fig. 1.

In this plant ore was usually unloaded from railroad cars into 1-ton mine cars, which ran over outside storage bins, Fig. 2, each capable of holding 50 tons of ore, and arranged for the installation of feeder-belt conveyors and trippers in the future. From the storage bins, which had

flat bottoms, the ore was shoveled or wheeled to an 18-in. belt conveyor running the length of the bin system in a concrete-lined pit. Shallow hoppers fed the conveyor in front of each bin. The ore-bin conveyor discharged on to an 18-in. conveyor running at right angles to it, and carried the ore up a slight incline discharging directly into a 9 by 15-in. (22.8 by 38.1 cm.) Blake crusher, which discharged the ore into an elevator pit. The elevator was inclined from the vertical about 15°, and had buckets 6 by 10 in. on a belt 12 in. wide. The elevator discharged

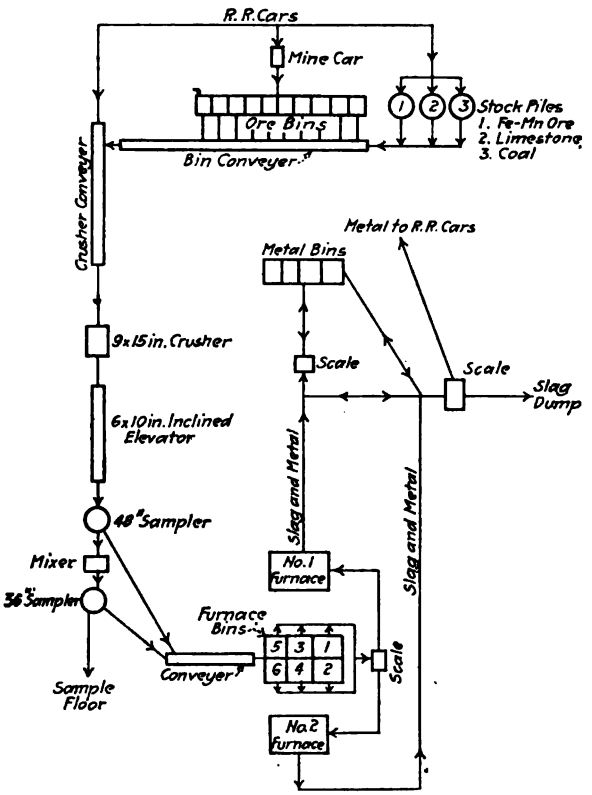

FIG. 1.—FLOW SHEET OF MATERIALS.

on to a 48-in. Snyder type sampler, which cut out one-tenth. The reject from the sampler was discharged on to a 14-in. distributing conveyor and tripper running at right angles to the elevator and over the furnace bins. The sample passed through a short conical mixing trommel and then to a 36-in. Snyder type sampler cutting one-tenth. The reject was discharge on to the distributing conveyor, while the sample fell to the floor below, where it was quartered. The reject from the sampler floor was shoveled into the elevator and discharged on to the distributing conveyor. Cars of ore that had been sampled in transit were not sampled

at the plant. Cars could also be unloaded directly on to the crusher conveyor. Cars that were to remain in storage were sampled by shovel, taking every tenth shovel.

FIG. 2.—STORAGE BINS.

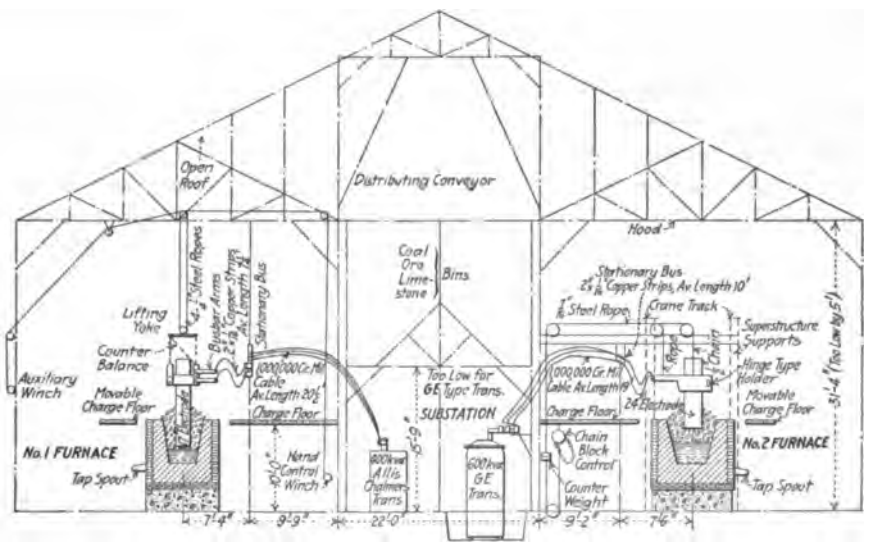

FIG. 3.—SECTIONAL ELEVATION OF PLANT.

FURNACE NO. 1—1200 KV-A.

Furnace

The furnace consisted of a rectangular steel shell 18 ft. long, 8 ft. wide, and 7 ft. deep made of ½-in. plate, riveted and stiffened with

channel iron, and rested upon four concrete piers. The three electrodes were hung from steel I-beams supported by the wooden trusses of the building. The furnace was operated with electrodes 17 in. (43 cm.) in diameter by 72 in. (182 cm.) long; some of them were threaded for continuous feeding and some were "butt" electrodes. When the furnace was started, it was impossible to obtain 17-in. electrodes, so 16-in., 14-in., and 8-in. were used. The load on the furnace was regulated by controlling the electrodes by hand. The sides and bottom of the furnace were lined with 8 in. (20.3 cm.) of firebrick, and this was lined with a mixture of calcined white California magnesite and hot pitch, which was tamped in place. There was no roof to the furnace, the charge level being left as high as possible; Fig. 3 is a section through the middle electrode and the tap hole. Metal and slag were tapped into pot cars through the same tap hole. The furnace was surrounded by a charge floor, which was level with the top, and was charged from bins that discharged on to this floor.

Transformers

Power was supplied to the furnace by three 400-kv-a., single-phase, Allis-Chalmers, oil-filled, self-cooled transformers of the following specifications: primary voltage, 13,200; secondary voltage, 75/37½; inherent reactance, 10 per cent., 2–5 per cent., primary taps.

The transformers were connected with coils in series delta-delta, with the primary sides on the 10 per cent. taps because of low line voltage, resulting in a voltage of 75 volts at the transformers. The secondary side was brought out of the transformer case as busbars. These transformers operated very satisfactorily, but on the hottest days in summer, with a load of 1100 kw., 85 per cent. power factor, there was a temperature rise of about 50° C., so air was blown against the case to prevent further rise.

Electrode Holders and Secondary Bus System

The electrode holders first used and the method of supporting the holders were based on the operation of furnaces taking electrodes up to 12 in. (30.5 cm.) in diameter, as these methods were satisfactory for the smaller furnaces. Although holder and cable troubles developed, the furnace was always operated at a profit and at over 78 per cent. average load factor. The holder on a smaller furnace, besides being subjected to less strain because of the smaller electrode, was not subjected to as high temperatures, because of the smaller volume of hot gases that passed from the furnace.

The requirements for a satisfactory holder are: Sufficient contact area between copper and carbon; mechanical strength; electrical conductivity; sufficient water cooling to prevent slipping and corrosion of the electrode

in the contact area; absence of copper to copper connection over the furnace or where there is exposure to hot gas; absence of small bolts or small threads which are not water cooled.

In the first holder used, shown in Fig. 4, the electrode was held by two levers, which forced the clamps against the electrode. The objec-

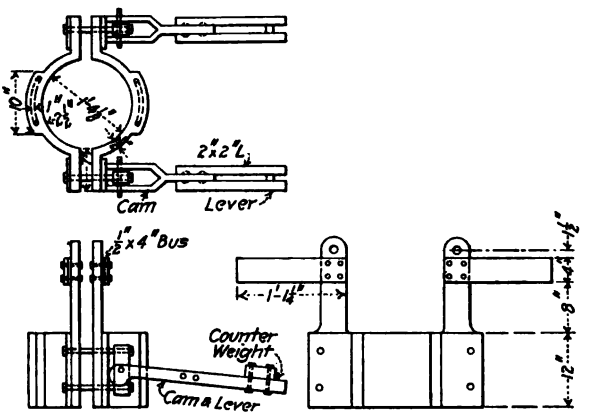

FIG. 4.—16-IN. LEVER-TYPE HOLDER, FURNACE NO. 1.

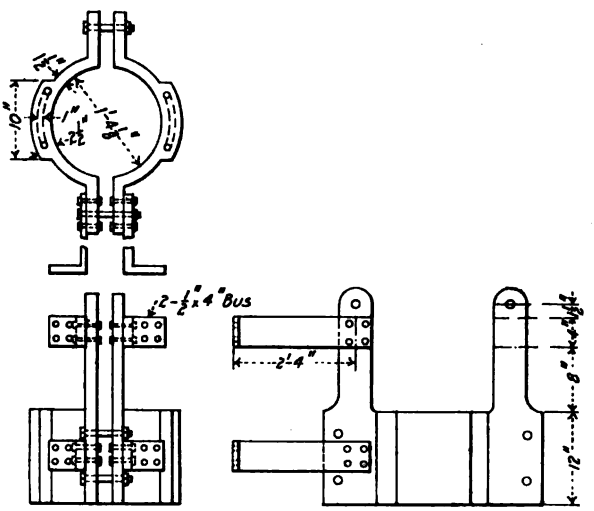

FIG. 5.—16-IN. BOLT TYPE HOLDER, FURNACE NO. 1.

tions to this holder were: The lever arms tended to swing together, causing short circuits; the pressure of the levers was so great that the holders were bent; there was short circuiting through the lever bolts between the two clamps; the holder was of too light construction and cracked after continued use; there was not sufficient water cooling; and as the connection beween the flexible cables and the holder was made

by bolting the cables to a short bus, which in turn was bolted to the holder, both connections being enveloped in the furnace gases, clean contacts could not be maintained because of shearing action of the busbar and cables at their contacts. These holders were installed with the two halves of each holder parallel to the long axis of the furnace, but after a

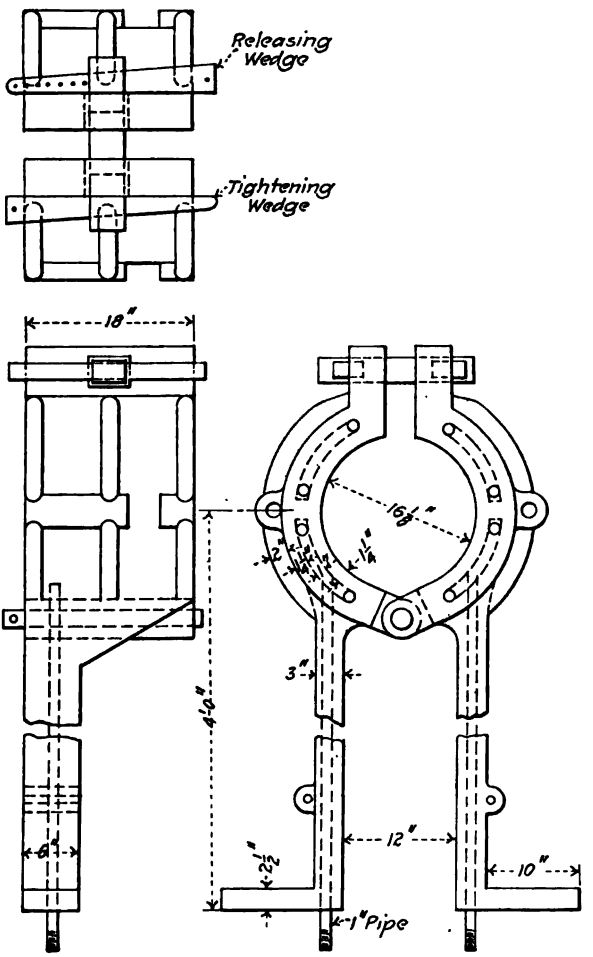

FIG. 6.—16-IN. HINGE-TYPE HOLDER, FURNACE NO. 1.

short period of operation the levers were replaced by bolts. This was not much of an improvement because of the shearing action at the contact between busbar and holder.

The second holder, shown in Fig. 5, differed from the first in that bolts and nuts were used instead of levers, and the connection of the flexibles to the busbar was placed farther from the hot part of the furnace. It

helped matters considerably but did not remove the difficulty of poor contact between busbar and holder, and whenever an electrode was changed or slipped it was generally necessary to cut the bolts. A considerably higher load factor was maintained with this holder, but continual repair work was required.

A third holder, shown in Fig. 6, met all the requirements, except that it was not strong enough on the front side, which later was strengthened by casting it with stiffening ribs. The holder was of the hinge type and consisted of two parts cast of 95 per cent. copper, with no busbar connection. The flexible connection to the holder arms was at the edge of the furnace shell. There were no bolts or levers, but three simple pins. It had a large water-cooled contact area. The contact area between the copper and the carbon was based on a load of 15 to 20 amp. per sq. in. of

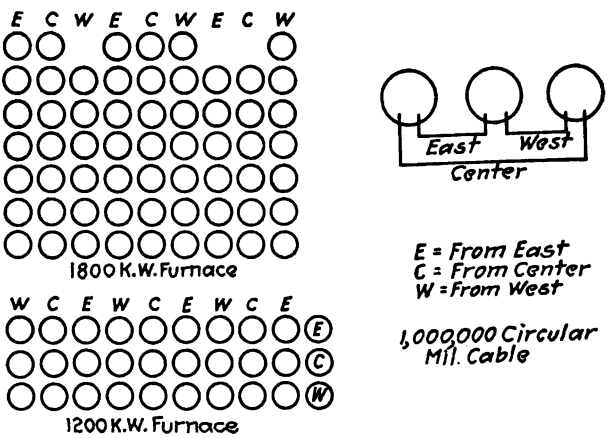

FIG. 7.—CABLE INTERLACING DIAGRAM.

maximum contact area with a perfect electrode. The holder was designed so that the area of one half of the holder would carry the complete load if required.

The system of holder suspension from I-beams supported on the roof trusses was unsatisfactory, although it works all right on small electrodes. At first, the holders were not counterbalanced, which resulted in their tilting at an angle dependent on the center of gravity of the electrode. The steel cables supporting the holders ran to sheaves on I-beam trolleys; these trolleys frequently failed to work because of the dust. The holders and the electrodes were eventually counterbalanced. The absence of a steel hood over the furnace resulted in fires, there being merely the usual foundry ventilator with louvers. An open-top furnace installed in a wooden building should always have a hood, especially when coal is used as a reducing agent.

The low-tension sides of the transformers were connected in delta.

From the delta connection over the transformers each phase was conducted to busbars at the furnace, as shown in Fig. 3, by ten 1,000,000 c.m. copper cables, with weatherproof insulation, to a phase. Dossert-connected lugs were used on the cable. The current was conducted from this point to the electrode holders by forty 0000 bare copper cables. The 1,000,000 c.m. cable was supported by insulator racks, and all phases were interlaced as shown in Fig. 7, up to about 2 ft. (60.9 cm.) from the point where connection was made to the flexibles. Due to their burning out, the 0000 flexible cables were replaced by copper strips 2 in. wide by 1/16 in. thick, 7 ft. 3 in. long (50.8 mm. by 1.59 mm. by 2.21m). These gave excellent results, eliminating all lugs in the furnace gases. Except where used over the furnace, the Dossert lugs gave fair satisfaction. After about four months continuous operation, the insulation on the 1,000,000 c.m. cables softened and ran down into the Dossert lugs on the connection at the delta bus, and caused bad contacts. On furnace No. 2 all lugs were replaced by welded connections. The loop from the delta connection on the transformers to the end of the electrode on furnace No. 1 consisted of 20 ft. 6 in. 1,000,000 cm. cable, 7 ft. 3 in. copper strips, 3 ft. 3 in. electrode holder, 4 ft. electrode, making a total length of 35 ft. (10.67 m.). The use of 1,000,000 c.m. cable instead of a busbar was fairly satisfactory and gave entire satisfaction on furnace No. 2, where welded lugs were used on the cable. Its main advantage was the ease with which complete interlacing of phases could be obtained. If a busbar had not been so difficult to obtain it would have been used.

Furnace No. 2, 1800 kv-a.

Furnace

The second furnace, Figs. 8 and 9, consisted of a rectangular steel shell 18 ft. long, 9 ft. wide, and 7 ft. deep, made of 1/2-in. (12.7 mm.) plate, riveted and stiffened with channel iron and resting upon four concrete piers. The three electrodes were hung from a steel superstructure, Figs. 3 and 9, that was entirely independent of the building. Over this superstructure ran a hand crane with an electric hoist, which was used for installing electrodes. The furnace was operated with electrodes 24 in. (61 cm.) in diameter, threaded for continuous feeding. The load on the furnace was regulated by hand control of the electrodes by chain blocks. The furnace was lined with an 8-in. (20.3 cm.) wall of red brick on the sides and bottom, and inside the brick, a lining was made by tamping in place a mixture of calcined white California magnesite and hot pitch, as shown in Fig. 3. There was no roof. Metal and slag were tapped into cars through the same tap hole. The furnace was surrounded by a charge floor that was level with the top, and was charged from bins that discharged on to the charge floor.

Transformers

Power was supplied to the furnace by three 600-kv-a., single-phase, General Electric, oil-filled, self-cooled, radiator-type transformers of the following specifications: Primary voltage 13,200; secondary voltage 75; inherent reactance about 7 per cent., 3–5 per cent. primary taps.

The transformers were connected delta-delta with the primary sides on the 10 per cent. taps, resulting in a voltage of 75 volts at the transformer. The secondary side was brought out of the transformer case as busbars, which projected 12 in. above the top of the transformer cover. This projection is not enough when three large single-phase transformers are connected in delta and the poles are interlaced; the bus in this case should have projected 24 in. If the secondary-delta bus

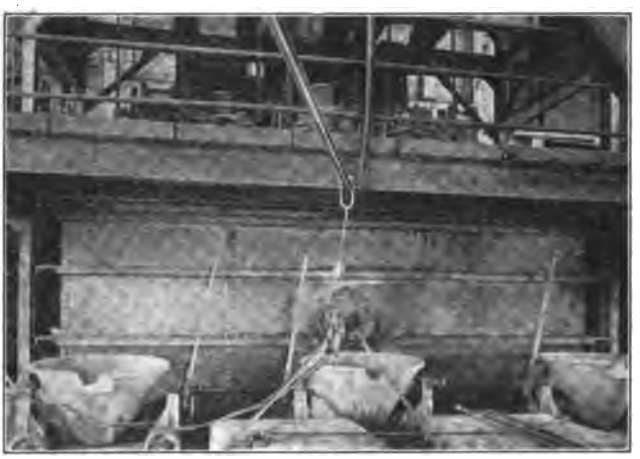

FIG. 8.—TAPPING FLOOR, FURNACE NO. 2, SHOWING POT CARS AND STINGER.

connection is within 8 in. (20.3 cm.) of the cover, heating results. If the transformer busbar is only 12 in. (30.5 cm.) long, either it must be built up 12 in. more, or an unsightly connection used. These transformers were operated with a load of 1100 to 1150 kw. and were never loaded to full capacity because of the condition of the ferromanganese market.

Electrode Holders and Secondary Bus System

The electrode holders of this furnace and their method of support gave excellent results. The electrode was held by a 24-in. hinge holder, Fig. 10, similar in design to the third type of holder used on furnace No.1 but of greater strength and lower copper content, 90 per cent. This holder gave entire satisfaction, and no trouble was experienced with the

holder or the flexible connections. The basis of design for current-carrying capacity was the same as for the furnace No. 1 holder.

By using the 3-ton electric hoist on the hand crane, electrodes could be slipped or replaced in 20 min. as compared with 1 hr. for changing electrodes on furnace No. 1, with hand-operated chain blocks and trolley. The framework was covered with a two-stack steel hood, which removed all furnace gases and reduced the danger of fire to a minimum

FIG. 9.—FRONT VIEW, FURNACE NO. 2, FROM CHARGE FLOOR. FURNACE IS EMPTY.

The low-tension sides of the transformers were connected in delta. From the delta connection over the transformers, each phase was conducted to a busbar at the furnace, as shown in Fig. 3, by twenty 1,000,000 cm. copper cables with weatherproof insulation. Welded connections were used on both ends of each length of cable. The current was conducted from the busbar to the electrode holders by copper strips

in. (5 cm) wide by $\frac{1}{16}$ in. (1.6 mm.) thick by 10 ft. (3.05 m.) long. The 1,000,000 cm. cable was supported by insulator racks, and all phases were interlaced up to about 2 ft. (61 cm.) from the point where connection was made to the flexibles, Fig. 7. Neither the welded lugs, the cable,

nor the strips gave any trouble during the operation of the furnace. One side of the loop from the delta connection on the transformer to the end of the electrode on furnace No. 2 consisted of 19 ft. of 1,000,000 cm. cable, 10 ft. of copper strips, a 4½-ft. electrode holder, and a 4-ft. electrode, giving a total length of 37 ft. 6 in. (11.4 m.).

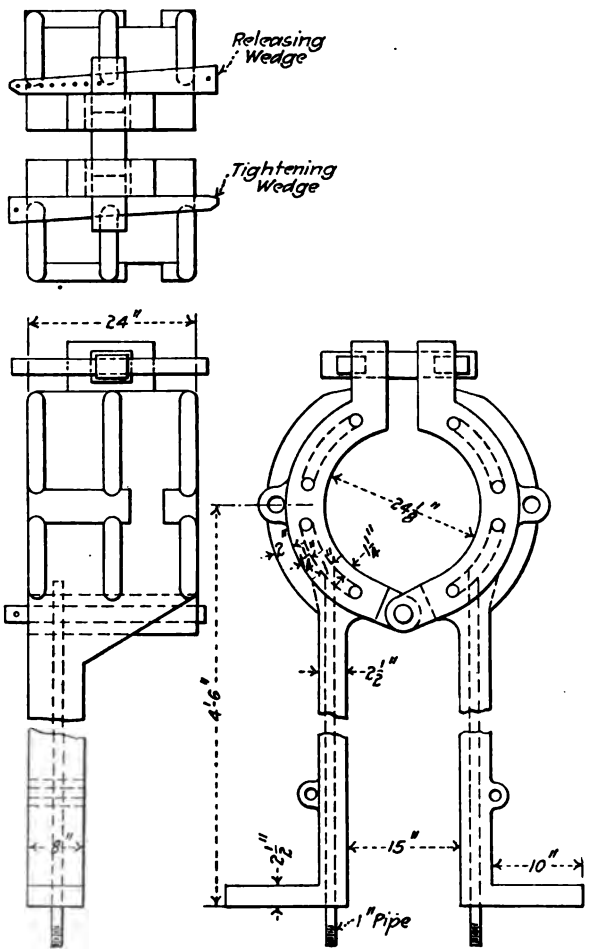

FIG. 10.—24-IN. HINGE-TYPE HOLDER, FURNACE NO. 2.

MANGANESE ORES

The ores used in the manufacture of ferromanganese, or furnace ores, are divided into two classes—oxide and carbonate. The first class is made up of pyrolusite, MnO_2, manganite, MnO(OH), hausmannite, Mn_3O_4, psilomelane, $MnO_2 + (H_2O.K_2O.BaO)$, wad, rhodonite, $MnSiO_3$, and braunite, Mn_2O_3. Domestic ores are a mixture of these oxides and as

such cannot be readily distinguished from each other. For practical purposes it is necessary to call them pyrolusite. Rhodonite is an undesirable ore that cannot be made into low-silicon ferromanganese. It is included here because the oxides are usually alterations of it, and it may be present in the mixture in varying quantities. When present, it usually passes into the slag without reduction. Rhodochrosite, $MnCO_3$, is mined on a large scale in only one locality, Butte, Mont. It has proved a desirable ore for electric smelting when mixed with oxide ore, but when smelted alone some difficulty has been experienced in maintaining a desirable output of metal.

For practical purposes oxide furnace ores are classified into: high-grade ore, which contains 35 per cent., or more, manganese with iron usually below 5 per cent., and low-grade ore, which contains from 10 to 35 per cent. manganese and from 10 to 25 per cent. iron.

The authors have used both steel turnings and ore containing 30 per cent. manganese and 10 per cent. iron for addition of iron to the charge when smelting high-grade ore containing little iron. The use of ore instead of turnings proved more satisfactory, because the furnace seemed to operate more uniformly and gave a greater output. The question of the use of iron ore or a manganiferous ore is one of costs.

Analyses of the ores smelted in obtaining the data given in this paper are shown in Table 3. Of these ores, the Ely ore smelted the most rapidly. After the use of steel turnings was abandoned, Leadville ore was charged to supply the iron. The combination of Ely and Leadville ores gave a mixture that smelted more rapidly than any other tried. The slowest smelting ore was the Las Vegas. This was due to its fineness, as the ore goes to a powder and resembles bog-iron ore, which resulted in furnace blows and a heavy dust loss. Because of the large proportion of coarse

TABLE 3.—*Domestic Manganese Ore from Colorado, Utah, and Nevada*

	Leadville, Colo.	Ely, Nev.	Las Vegas, Nev.	W. Tintic, Utah	Green River, Utah	Composite Sample Dry Ore to Furnace, 1918		
						October	November	December
Mn, per cent....	33.10	42.12	37.48	38.92	40.88	35.49	34.54	34.9
SiO_2, per cent...	11.55	15.42	14.0	13.3	11.33	13.9	12.8	13.0
MgO, per cent ..		trace	2.04	trace		0.27	0.24	0.65
Fe, per cent.....	11.7	2.65	1.33	4.26	2.37	7.42	8.11	5.71
CaO, per cent...	1.6	7.94	1.29	0.80	tr	5.34	4.23	7.65
Al_2O_3, per cent..	12.92		1.06	3.96	2.64	3.42	3.26	2.31
P, per cent.....	0.066	0.023	0.028	0.022	0.056	0.052	0.033	0.03
S, per cent.....	0.109	0.081	1.23	0.052	0.51	0.53	0.73	0.58
BaO, per cent...						3.05	2.66	1.92
PbO, per cent...	4.7					present	present	present
Zn, per cent.....	trace							
Cu, per cent ...	none							
H_2O, per cent...	12.6	5.65	14.0	13.2	2.3			
CO_2, per cent ..						5.00	7.22	9.0

material, Leadville ore is fast smelting. The difficulties of operating this plant were considerably increased by the fact that it was necessary to change the charge almost every day, because the ore was so variable, coming from several properties, and with such a small operation, bedding did not seem practical.

Reducing Agents and Fluxes

Several reducing agents have been used in electric smelting of manganese ores, and although lignite and bituminous coals were considered the best during the war, the operating results of one producer show that coke can be used satisfactorily. The supposedly essential characteristics of a good reducing agent are a high ratio of fixed carbon to ash, minimum quantity of highly combustible gases, and low electrical conductivity. Table 4 gives the analyses and ratios of carbon to ash of reducing agents available in Colorado.

Table 4.—*Colorado Reducing Agents*

	Moisture, Per Cent.	Volatile Matter, Per Cent.	Sulfur, Per Cent.	Carbon, Per Cent.	Ash, Per Cent.	Ratio Carbon to Ash
Segundo coke	0.68	1.7	0.6	81.8	16.5	4.9
Crested Butte, anthracite slack	0.68	7.82	0.84	81.7	9.83	8.3
Crested Butte, anthracite slack		6.62	0.63	78.9	14.18	5.6
Crested Butte, anthracite No. 6		7.4		82.76	10.2	8.2
Crested Butte, anthracite No. 6		5.87		84.15	9.98	8.4
Leyden nut, lignite coal	13.84	36.42		44.84	4.9	9.0
Leyden, mine run, lignite coal	13.0	36.44		44.53	6.03	7.4
Matchless, lignite coal	46.46			43.4	10.2	4.3
Oak Creek, lignite coal	6.69	25.6		53.39	14.32	3.7
Berwind, lignite coal	1.66	41.71		45.88	10.75	4.3
Sopris, bituminous coal	1.26	33.64		51.57	13.53	3.8

The commonly used fluxes are limestone and lime. Limestone low in phosphorus and magnesium is desirable. On the whole limestone is preferable to lime, as lime is difficult to hold in storage bins because of slacking and expansion. It slacks so easily that after a short period of storage the CaO content has changed, and the slag analysis varies because of uncertainty as to the exact quantity of CaO being charged.

Calculation of Charge

In commercial operation, a complete charge calculation serves only as a guide in starting up the furnace, because coal, limestone, and the iron-bearing material are varied in the quantities experience has shown to be best in order to produce metal of the manganese and silicon content desired and a slag containing 10 to 15 per cent. manganese. E. S. Bardwell[2] has given a typical theoretical charge calculation.

[2] E. S. Bardwell: Electric Furnace Smelting of Montana Manganese Ores. *Chem. and Met. Eng.* (1920) **22**, 681.

For use when the iron in the charge is supplied by a manganese ore comparatively low in manganese and high in iron, some curves have been

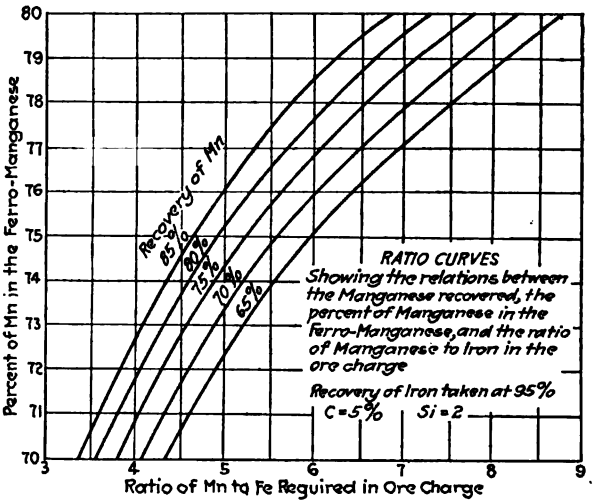

FIG. 11.—CHARGE CALCULATION CURVE, MANGANESE-IRON RATIO.

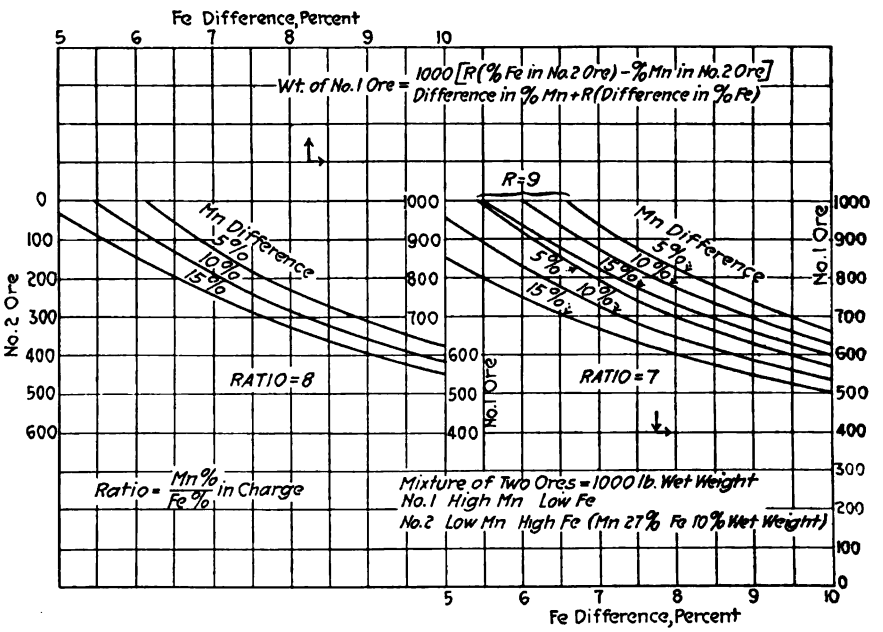

FIG. 12.—CHARGE CALCULATION CURVE, ORE PROPORTIONS.

developed, which aid in quick charge calculation. The curves shown in Fig. 11 provide a quick means of determining the ratio of manganese

to iron required in the charge for production of ferromanganese of a certain grade, considering the approximate recovery of manganese being made at the time.

Having determined the ratio of manganese to iron, the proportions of any two ores required to give the desired grade of ferromanganese can be determined from the curves shown in Fig. 12 where No. 1 ore is a high-grade manganese ore with low iron content, and No. 2 ore is a low-manganese high-iron ore. Or the proportions can be found from the following formulas in which the total weight of the mixture is 1000 lb. (453.6 kg.). Weight of No. 1 ore =

$$\frac{1000\,[R\,(\text{per cent. Fe in No. 2 ore}) - \text{per cent. Mn in No. 2 ore}]}{\text{Difference in per cent. Mn} + R\,(\text{difference in per cent. Fe})}$$

This formula is developed as follows, letting weight of mixture be 1000 lb.

A = high-grade ore, No. 1, in pounds;
B = low-grade ore, No. 2, in pounds;
x = per cent. manganese in No. 1 ore;
y = per cent. iron in No. 1 ore;
z = per cent. manganese in No. 2 ore;
w = per cent. iron in No. 2 ore;

$$R = \frac{\text{Total manganese in mixture}}{\text{Total iron in mixture}}$$

Then

$$R = \frac{Ax + Bz}{Ay + Bw}$$

$$B = (1000 - A)$$

$$Ax + Bz = RAy + RBw$$

$$Ax + z\,(1000 - A) = RAy + Rw(1000 - A)$$

$$Ax + 1000z - Az = RAy + 1000Rw - ARw$$

$$Ax - Az - RAy + ARw = 1000Rw - 1000z$$

$$A(x - z - Ry + Rw) = 1000(Rw - z)$$

$$A = \frac{1000\,(Rw - z)}{x - z - Ry + Rw} = \frac{1000\,(Rw - z)}{x - z + R\,(w - y)}$$

$$A = \frac{1000\,[R(\text{per cent. Fe in No. 2 ore}) - \text{per cent. Mn in No. 2 ore}]}{\text{Difference in per cent. Mn} + R(\text{difference in per cent. Fe})}$$

Method of Operation

Furnace No. 1 was operated for about 8 mo. with an average load of 1100 kw. measured on the primary circuit, and at a secondary voltage of 70 to 75 volts at the furnace. Except for difficulty with the faulty holder design and the time required for changing electrodes, there was little operating time lost and the electrical load factor averaged 78 per cent. for the 5 mo. electrodes were available for full monthly operation. The power factor was 85 per cent.

Furnace No. 2 was operated for about 1½ mo. with an average load

of 1100 kw. measured on the primary circuit, and at a furnace voltage of 70 to 75 volts. With the improved electrode holder design and 24-in. electrodes instead of 17-in. electrodes, as on furnace No. 1, a high load factor was obtained. The electrical load factor was 85.1 per cent., and the furnace operated 96.4 per cent. of the total time; this improvement was due to the better mechanical arrangement for changing electrodes, no holder troubles, and the lower electrode consumption requiring fewer changes of electrodes.

The furnace was charged and tapped every 2 hr. Ore, coal, and limestone were drawn from the bins feeding onto the furnace floor, where they were weighed and spread mixed. All of the charge for a 2-hr. period was charged immediately after tapping, which is contrary to the practice in most plants where the furnaces are charged at about 15-min. intervals and poked often. The maximum size of the ore was about 2½ in. (63.5 mm.) with a large percentage of fine material. Nut lignite coal was used. When anthracite was charged, it was either slack (mostly dust) or No. 6, which is the ¾-in. size. The lime rock was crushed to 2½ in. Metal and slag were tapped at 2-hr. intervals through a common tap hole into pot cars. The tapping was done by driving a bar into the hole and then driving it back out; at times it was necessary to use either an electric "stinger," Fig. 8, or oxygen.

Difficulties of Furnace Operation

Although the electric smelting of manganese ores is not difficult, from the metallurgical standpoint, in that the grade of the product can be readily controlled, several operating difficulties may arise: Formation of carbides in furnace, blowing, failure of bottom, tapping, failure of electrode holders, and bridging of charge.

Formation of Carbides in Furnace

Formation of carbide in electric smelting of manganese ores for production of ferromanganese is common and may be expected at any time. No other metallurgical condition results in greater operating troubles. The presence of carbide is shown by the odor of acetylene when the slag is dropped in water, by crusts rising in the furnace and collecting around and under the electrodes, by difficulty of tapping, and by either a thick slag or a foamy slag. In placing new plants in operation, the common error has been to attempt to produce a slag low in manganese, 5 per cent., by operating with a considerable excess of reducing agent and a high-lime slag. The combination of considerable excess coal and sufficient lime to give a slag containing much over 40 per cent. CaO invariably results in the formation of carbide. By operating with such a charge a 5 to 8-

per cent. manganese slag will be produced for several days, but before a week has passed the furnace is usually full of carbides, so that it can be tapped only with great difficulty, and there is a marked reduction in the output of metal. The electrodes tend to climb out of the furnace, because of the accretions of carbide that have formed beneath them, and the metal freezes on the bottom of the furnace. The authors found that continuous charging resulted in a greater tendency to formation of carbide than intermittent charging, and that carbide formed more readily with anthracite than with bituminous coal, and more readily with bituminous coal than with lignite. When carbide is forming in large quantity in the furnace, there also appears to be considerably greater volatilization of manganese. Carbide does not, however, affect the total percentage of manganese recovered to any extent, because the increased volatilization loss seems to be offset by the lower slag loss. A partial solution of the carbide difficulty was made by the following procedure:

1. Use of lignite instead of anthracite or bituminous coal.
2. Reducing the quantity of coal to slightly above the theoretical requirement, and reducing the quantity of limestone in the charge, so that the slag contains 12 to 15 per cent. manganese, and about 40 per cent. CaO plus MgO.
3. When carbide forms in spite of the above precautions, the use of a flushing charge containing the usual quantity of all ingredients except coal, which is reduced to one-half the usual quantity.

The operating data compiled in Table 5 show, in a general way, the results of changing from anthracite to lignite, the effect of operation with a lower lime slag, and the effect of flushing charges. So many variables enter into data obtained from plant operation that the cause of the increased production during the last four months of operation cannot be assigned to any one cause, but must be considered as due to the combination.

Blowing

By "blowing" is meant eruptions in the furnace caused by the accumulation of gas in the charge, which escapes under high pressure and burns on the top of the furnace. With an open porous charge, this would not occur to any extent and is not serious in the manufacture of ferrochrome or ferrosilicon, where coke is generally used as a reducing agent. The blows of a manganese furnace operated with coke should not be serious, but with coal as a reducing agent, at times they are very serious. Carbon monoxide from reduction accumulates in pockets with gradually increasing pressure, and as manganese ore is generally fine and dusty the charge packs, so that the gas cannot escape until its pressure forces it out of the charge. The charge may be blown 25 ft. above the furnace, carrying with it fine particles of coal, which ignite and cause a mass of

flame over the furnace. This may cause the suspension chains of the holders to break, and will eventually cause trouble with the holders if there is any copper-to-copper connection over the top of the furnace. There is a considerable loss of manganese in dust and volatilization at each blow.

The authors started their operation on the Las Vegas ore, of the analysis given in Table 3, with slack Colorado anthracite as the reducing agent. This ore is of the bog type and when crushed goes to a powder that is unusually light and dusty. This ore was smelted during May, June, and July. In combination with the fine anthracite charged during May and June, the furnace was blowing a large part of the time, which together with the formation of carbide resulted in a low output. The unaccounted loss, or dust and volatilization, amounted to an average of 26.9 per cent. of the manganese charged. Considerable of this loss was due to the dusty character of the ore, as slack anthracite was used in January on a coarse ore, for economic reasons, when the unaccounted loss was 12.1 per cent. When nut lignite was used the blows were much less serious. Except for its tendency to form carbide and its high cost, coarse anthracite would probably have helped to stop blowing more than the nut lignite, which always contains fine material due to slacking before use. This fine coal was screened out on the charge floor.

The authors found that the most satisfactory results, from the viewpoint of carbide formation, blowing, and labor costs, were obtained by charging the furnace full after a tap and not touching it except in case of a bad blow until after the next tap. Continuous charging and poking tended to aggravate the blowing. This seemed to be due to the fact that the furnace could not get settled in any fixed condition of smelting, and the poking of the charge into a hole, with possibly molten material at the bottom, always started a blow.

The fundamental cause of blowing in a ferromanganese furnace is the nature of the charge. Manganese ores contain a large percentage of fine materials; particularly rhodochrosite, which decrepitates and goes to a powder in the furnace, giving off a large volume of CO_2, which increases the blowing. Flame has been observed to blow to a height of 50 ft. for several minutes from the top of a 3500-kw. furnace, smelting rhodochrosite with semi-bituminous coal as a reducing agent.

Failure of Bottom

To the knowledge of the authors only three materials have been tried for furnace bottoms—carbon, dead-burned or calcined magnesite, and firebrick. The carbon bottom is used at Anniston, Ala., and Bay Point, Calif. The magnesite bottom was used at Utah Junction, Colo. At Great Falls, Mont., both carbon and magnesite have been used. It is reported that ordinary firebrick was used at Heroult, Calif.

One plant reported that the carbon bottoms failed every 2 or 3 mo. until the furnace shell was elevated high enough above the floor to allow air cooling. The magnesite bottoms installed by the authors never failed. One was in continuous use for 8 mo. and the other 1½ mo. The first magnesite bottoms installed in another plant were in use for several months and did not fail until the cross-section of the electrodes was reduced one half, so that the full load of the furnace was put through the reduced section, thus overloading them 100 per cent. It is understood that the firebrick bottom tried at Heroult, Calif., was satisfactory, but little information regarding it is available.

Theoretically magnesite should make the best bottom. The slag formed in smelting manganese ore must be essentially basic, because if it is acid manganese acts as a base and substitutes for the deficiency in lime. Also magnesite does not easily form combinations with manganese or carbon. On the other hand carbon combines with manganese to form manganese carbide, with lime to form calcium carbide, and with the oxygen in the ore. The failure of carbon bottoms is probably due to a combination of these reactions, but may be due to careless operation of the furnace and lack of air cooling, factors that would influence the length of life of all linings, if they affect the life of one.

Careless furnace operation has probably ruined many bottoms, particularly in large plants. In open-top furnaces, there is a tendency for craters to form under each electrode, due probably to the intense heat at the end of the electrode. These craters fill with molten metal, which remains there. If the crater gets too deep, the bottom will go. Whenever the electrodes are riding low in the furnace and a considerable depth of molten metal is below the level of the tap hole, an attempt should be made to freeze this metal, either by variation of the charge so as to cause the electrodes to rise, or by throwing off the power until it freezes. The authors have had under the electrode pools so deep that only a foot of bottom was left, and have not lost the bottom.

When installing a magnesite lining, only enough pitch should be used to make the magnesite stick together. The bottom of the crucible should be about 1 ft. (30.48 cm.) above the top of the tap hole level, as it will drop about 1 ft. when the pitch burns out. The sides should be built of magnesite only for about 2 ft. above the bottom of the crucible, and capped with firebrick, because the magnesite on the sides tends to cave.

Tapping

Tapping is apt to be difficult when there is considerable carbide in the furnace and when the electrodes are riding high; at other times the hole can generally be opened without much trouble. A better method of tapping than driving the hole was recently observed at one plant. The

bar is driven into the hole immediately after tapping and plugging and is left there until the next tap; then driving it out usually opens the hole without much sledging or the use of oxygen.

Tapping metal and slag into pots, which are allowed to cool before dumping, effects considerable saving in labor over tapping on to the floor or pouring from a ladle on to a casting machine; the metal is better in appearance and is more free from slag. The labor saving is in the men required for cleaning the metal. When metal and slag are tapped into a ladle, the slag skimmed, and the metal poured on to a casting machine, there is a high percentage of skulls and dirty slag, which must be concentrated by wet methods. This is avoided in pot casting, when the slag containing metal is such a small proportion of the total slag tapped that it can be charged back into the furnace daily. It will average less that 10 per cent. of the weight of uncleaned metal tapped. The increased labor of floor casting or machine casting over pot casting is due to the fact that the pot-cast metal is in large chunks, so that it can be more easily cleaned and sorted; also, no labor is required for wet concentration of skulls and dirty slag. One man can clean and sort about 10 gross tons of pot-cast metal per 8-hr. day.

The pots used for pot tapping were made of cast iron. At first many pots were lost, but during the last 4 mo. of operation the loss was very small. The burning out of pots is due to filling them too full of metal, which results in softening the iron in the pot so that a hole is burned through at some point. By filling the pot only two-thirds full, this is avoided and the life of the pot is greatly increased. Where a cast-iron ladle is set in a pit under the runner, and the metal and slag fall about 6 to 8 ft., it is necessary to put a slag bottom in the pot, or it will burn through. When tapping into pot cars, the metal fell only about 2 ft. so that only a fireclay wash was necessary.

Failure of Electrode Holder

Failure of electrode holders is usually due to defective design and to imperfect electrodes. The design of a holder may be faulty in three respects: The holder has a copper-to-copper connection over the top of the furnace; there is not sufficient contact area between copper and carbon; and the design is not sufficiently rugged and bends out of shape under heavy usage or when clamping an undersize electrode.

Improper design has been due to failure to recognize the difference between conditions on the top of the electric manganese furnace and the electric steel or other ferroalloy furnaces. The top of the electric steel furnace is cool, and a holder in which horizontal busbars are bolted to the electrode clamps works satisfactorily. The electrode holder is not continually exposed to the heat and flame that rise above the top of the manganese furnace and envelop the holder. The ferrochrome furnace is

not nearly as hot above its top as the manganese furnace and seldom blows. The electrode holder of the ferromanganese furnace should contain no busbar; instead an arm should be used which is cast with one side of the clamps, so that the holder consists essentially of two pieces, as shown in Fig. 10. The contact area between copper and carbon should be figured on a basis of carrying not to exceed 20 amp. per sq. in. The walls of the holder should be well reinforced with ribs to prevent bending, as much time is lost in slipping electrodes into a warped holder. The walls of the holder around the electrode should be cored and complete water cooling provided. Lack of sufficient water cooling at the clamps causes slipping of the electrode in the holder and arcing between the holder and the electrode. It is preferable that the holder be hinged, as it eliminates the use of one bolt or of a pin-and-wedge connection. The authors prefer the pin and wedge on a moderate size furnace as it is simpler and if properly designed seldom gives trouble. If a bolt is used, it should be water cooled or of large dimensions.

Bridging of Charge

Bridging of the charge between the electrodes is caused by the electrodes being spaced too far apart. When furnace No. 1 was started the electrodes were spaced on 5-ft. (1.5 m.) centers but the charge bridged so that metal and slag under the end electrodes could not be tapped. The electrodes were then spaced on 4-ft. centers and later were spaced on 3½ ft. centers, then there was no bridging. The electrodes on furnace No. 2 were spaced on 3½-ft. centers when the furnace was started and the charge never bridged.

Operating Results of Manufacture of 70 to 80 Per Cent. Ferromanganese in a 1100-kw. Furnace

The results of smelting 6,355,311 lb. (2882.7 T.) of manganese ore in an 1100-kw. furnace of the type described, with the production of 2,083,818 lb. (945.2 T.) of ferromanganese, are shown in Tables 5, 6, and 7. In drawing conclusions from these tables it must be remembered that these are plant operating results with several variable factors. In May, due to shortage of electrodes, four 8-in. diameter electrodes were used per holder instead of 16-in. electrodes; 16-in. electrodes were used in June and July. In August, September, October, November, and December, 14-in. and 17-in. electrodes were used. In December, at about Christmas, the operation of furnace No. 1 was stopped, and furnace No. 2 started with the same power input, but with 24-in. electrodes. Some of the 14-in. and 17-in. electrodes were "butt" electrodes, and some were threaded; the other sizes were threaded. The electrodes were of four brands. During all of May and June and part of July, the required iron

was supplied by steel turnings. Late in July, Leadville iron-manganese ore was substituted for the turnings. Anthracite was used entirely in May and for the greater part of June. After that nut lignite was the reducing agent, except in January, 1919, when anthracite was again charged in order to consume the stock on hand. Limestone was the flux in May, June, December, and January. In the other months both limestone and lime were charged. In July, the furnace was shut down seven days because of lack of electrodes, in August three days, and in September seven days. The grade of ore gradually dropped from 39.1 per cent. manganese, in May, to 34.25 per cent., in January.

Table 5 shows the metallurgical results; Table 6 shows the consumption of furnace supplies; and Table 7 the power consumption. These tables are to be used as a whole, because the information contained is for the same period. Analyses of the anthracite and Leyden lignite used are given in Tables 4 and 9. Table 9 shows the analyses of the limestone and lime. Tables 3 and 9 give the ore analyses.

All power was measured on the primary circuit and the figures given include furnace, motor, lighting, and laboratory loads, which are designated here as "plant." The power consumption outside of the furnace load is conservatively estimated at 10,000 kw-hr. per mo. In Table 10, a deduction of 10,000 kw.-hr. per mo. has been made in figuring the power consumption of the furnace only, designated as "furnace."

The operating results of October, November, and December are representative of what can be expected metallurgically. A higher time operating efficiency, load factor, and lower electrode consumption can be obtained, as was demonstrated in January, but this month is not included because anthracite was the reducing agent.

The gradual decrease in percentage of manganese in the ore charged to the furnace was partly due to an actual drop in the high-grade ore and partly to the use of Leadville ore. There was no apparent difference in power consumption when smelting the lower grade ore, or when producing 70 per cent. ferromanganese instead of the 80 per cent. grade. This was probably due to varying furnace conditions.

The effect of changing the reducing agent from anthracite to lignite was the increased recovery resulting from the change. The use of anthracite in January, after the furnace operation was thoroughly established, resulted in a recovery of 65.4 per cent. of the manganese, compared with 75.5 per cent. recovery in December with lignite. The average manganese recovery for the three months operation with anthracite was 60.1 per cent., the average recovery for six months of operation with lignite was 71.1 per cent. The conclusion may be drawn that the use of lignite in the electric furnace production of ferromanganese results in a 10 per cent. higher recovery than when anthracite is the reducing agent.

TABLE 5.—*Metallurgical Data: Furnace No. 1, May 1 to Dec. 26, 1918; Furnace No. 2, Dec. 26, 1918, to Jan. 31, 1919*

	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.
Charge:									
Manganese ore, high grade, pounds	514,011	632,148	533,629	531,121	573,380	441,968	364,308	567,419	510,042
Manganese ore, Leadville, pounds						446,863	547,504	225,228	487,690
Coal, anthracite, pounds	133,325	124,650							240,760
Coal, lignite, pounds		40,797	253,673	267,690	365,975	408,900	334,800	381,300	19,300
Limestone, pounds	202,075	202,300	146,304	73,365		178,800	80,130	162,547	207,180
Lime, burnt, pounds			5,065	62,275	79,490	12,920	77,400		
Fluorspar, pounds	7,170				390				
Steel turnings, pounds	14,170	20,930	5,970					400	
Average analysis of ore, dry, Mn, per cent	39.1	39.75	39.35	37.6	38.2	35.49	34.54	34.9	34.25
Average analysis of ferromanganese:									
Manganese, per cent	80.0	79.0	78.8	78.75	80.2	74.5	70.8	75.2	72.3
Silicon, per cent	3.17	2.53	2.78	1.44	2.68	2.21	2.18	3.39	1.57
Sulfur, per cent	0.004	0.004	0.024	0.02	0.007	0.013	0.012	0.008	0.023
Phosphorus, per cent	0.11	0.18	0.20	0.22	0.15	0.10	0.11	0.09	0.15
Average analysis of slag:									
Manganese, per cent	12.1	12.85	9.14	11.0	9.78	11.36	12.98	12.2	14.44
SiO_2, per cent	27.8	28.1	29.0	31.4	29.8	27.7	28.7	29.3	29.7
CaO, per cent	39.2	39.0	40.6	38.5	41.5	39.2	36.9	37.2	35.2
MgO, per cent	5.3	3.2	3.1	2.9	3.5	2.3	2.0	2.8	2.1
Al_2O_3, per cent	9.5	9.7	12.5	10.0	8.6	7.5	8.2	7.9	8.5
Ferromanganese, pounds	144,684	182,970	174,700	191,609	193,827	311,180	298,125	278,007	308,716
Ferromanganese, gross tons	64.6	81.7	78.0	85.5	86.5	138.9	133.1	124.2	137.8
Slag, pounds	234,337	294,189	217,845	247,180	225,612	365,042	385,640	372,059	531,875
Ratio ore to metal	3.55	3.45	3.05	2.77	2.95	2.85	3.05	2.85	3.16
Slag per gross ton metal, pounds	3,627	3,600	2,792	2,892	2,608	2,626	2,890	2,995	3,859
Slag per net ton metal, pounds	3,241	3,215	2,492	2,580	2,328	2,347	2,588	2,676	3,446
Total manganese in metal, per cent	57.5	57.5	65.8	75.4	70.2	73.45	67.0	75.5	65.4
Total manganese in slag, per cent	14.1	15.0	9.5	13.6	10.0	13.15	15.85	16.28	22.5
Total manganese unaccounted, per cent	28.4	27.5	24.7	11.0	19.2	13.55	17.15	8.22	12.1

NOTE.—All weights are weights as weighed. Phase voltage 70–75 volts Average load on furnace about 1100 kv-a.

TABLE 6.—*Consumption of Furnace Supplies*

	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.
Electrodes, pounds	26,477	24,504	22,257	23,596	20,139	26,779	24,811	28,457	19,415
Electrodes per gross ton metal, pounds	409.8	300	285.3	277	232	193	186.5	229	141
Electrode used, diameter inches	16–8[a]	16	16–14	14–17	14–17	14–17	14–17	14–17–24	24
Electrode paste, pounds	300	200	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Electrode paste per gross ton metal, pounds	4.6	2.4							
Tapping steel, pounds	2,124	3,347	2,318	1,074	1,349	1,722	4,786	2,011	1,273
Tapping steel per gross ton metal, pounds	33.1	40.9	29.8	12.5	15.6	12.3	36.3	16.3	9.3
Oxygen, cubic feet	None	2,000	2,000	2,000	800	None	None	400	None
Oxygen per gross ton metal, cubic feet		26.9	25	23.4	9.2			3.2	
Magnesite, pounds	None	None	None	675	3,152	None	None	None	None
Magnesite per gross ton metal, pounds				8	36.5				
Fireclay, pounds	5,531	4,687	2,202	8,000	8,370	11,818	13,275	8,765	9,353
Fireclay per gross ton metal, pounds	85.6	57.3	28	93.5	97	85	99.5	70.5	68
Pitch, pounds	None	None	None	275	1,225	None	None	None	None
Pitch per gross ton metal, pounds				3.2	14				

[a] 16-in. electrode not available, used 4–8-in. electrodes per holder. [b] Included in weight of electrodes.

TABLE 7.—*Power Consumption*

	May [a]	June [a]	July [a]	Aug.[b]	Sept.[a]	Oct.	Nov.	Dec.	Jan.[c]
Maximum 1-hr. demand, kilowatts	1135.1	1181.6	1259.8	1191.8	1,155	1,145	1130.2	1142.2	1,175
Total kilowatt-hours consumed,[d] plant	605,200	653,000	527,400	515,000	462,800	706,800	643,800	656,600	745,400
Plant load factor, per cent	72.2	76.7	56.3	58.8	55.2	82.5	79.1	79.9	85.1
Percentage of time operated				72.3	64.8	88.6	86.2	85.3	96.4
Furnace days operated				22.4	19.4	27.4	25.9	26.4	29.9
Metal per calender day, pounds	4,667	6,099	5,635	6,180	6,460	10,038	9,937	8,967	9,958
Metal per furnace day, pounds				8,554	9,990	12,800	12,510	11,050	10,620
Kilowatt-hours per gross ton metal,[d] plant	9,368	8,000	6,770	6,100	5,330	5,070	4,830	5,280	5,420
Kilowatt-hours per short ton[d] metal, plant	8,380	7,130	6,040	5,375	4,780	4,640	4,310	4,730	4,890

(*a*) Shut down 7 days, no electrodes.
(*b*) Down 3 days, no electrodes.
(*c*) Using anthracite coal.
(*d*) Includes miscellaneous plant power, approximately 10,000 kw.-hr. per mo.
All power measurements made on primary side of transformers.
NOTE.—Average load on furnace about 1100 kw. Phase voltage 70 to 75 volts.

The use of lime instead of limestone did not result in a lower power consumption as it should do theoretically; this was probably due to the limestone being calcined on the top of the furnace by heat which otherwise would be wasted.

The furnace voltage during the last four months of operation was 70 to 75 volts and in May and June, it was 75 to 80 volts; there appeared to be a considerably higher volatilization loss at this time. When the voltage was increased to 120 volts for several days, the volatilization was marked, and the furnace load was difficult to control. A voltage of 65 to 75 volts seems to be satisfactory for a 1100-kw. furnace.

The recovery of manganese during the last quarter of 1918, in which the smelting practice was thoroughly established and it was possible to operate for a full month, averaged 72 per cent. Of the loss, 28 per cent., 15 per cent. was in the slag and 13 per cent. unaccounted loss. The average slag volume was 2830 lb. (1283.7 kg.) of slag per gross ton of metal. The percentage manganese in the slag averaged 12.2 per cent. As this proved to be about as low an average slag as could be produced without excessive formation of carbide and a decrease in output, the recovery on this ore cannot be increased except by reduction of the unaccounted loss, which might be accomplished by lowering the voltage or briquetting the fine ore. The average recovery over the nine months period of operation, including good and bad months, was 68.6 per cent. Of the loss of 31.4 per cent., 13.4 per cent. was in the slag and 18.0 per cent. unaccounted loss. The average slag fall for the nine months was 3121 lb. of slag per gross ton of ferromanganese.

The average "plant" power consumption for the last quarter of 1918 was 5066 kw.-hr. per gross ton of ferromanganese, or 4524 kw.-hr. per short ton. The average "furnace" power consumption was 4990 kw.-hr. per gross ton or 4457 kw.-hr. per short ton of ferromanganese. This power consumption can be met regularly with the grade of ore smelted: 34.94 per cent. manganese and 13.2 per cent. SiO_2, in an 1100 kw-hr. furnace. It is possible that a lower power consumption would have resulted in January except for the use of anthracite instead of lignite. The average "plant" power consumption for the whole nine months of operation was 6240 kw.-hr. per gross ton of ferromanganese or 5586 kw.-hr. per short ton.

For the four months after September, until it was closed down, the "plant" operated at an electrical load factor of 81.6 per cent.; the "furnace" load factor would be a little higher than this. The average percentage of time operated was 89.1 per cent. The power factor, as determined by the power company, varied between 85 and 90 per cent. This load factor was attained with hand operation of electrodes. Some typical load curves are shown in Figs. 13 and 14. If operations had been continued the load factor would have averaged 85 per cent., and

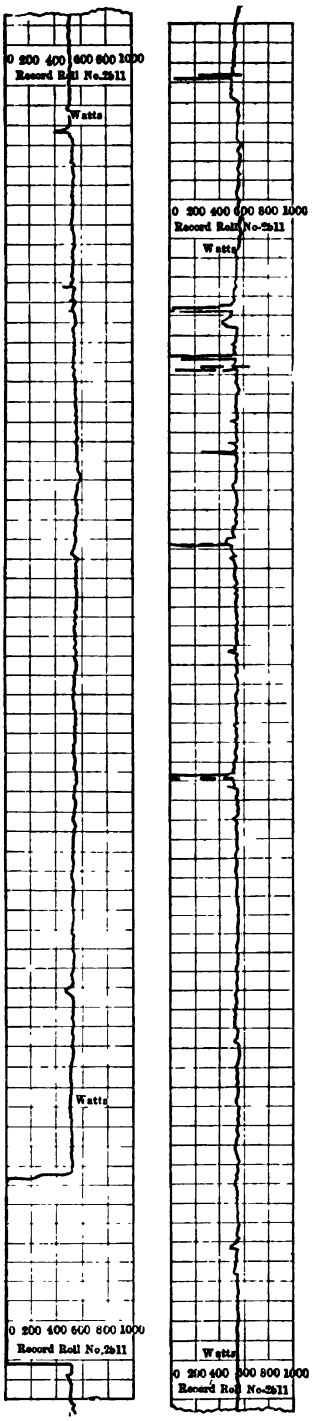

FIG. 13.—24-HR. LOAD CURVE OF FURNACE NO. 1. $K = 1.92$.

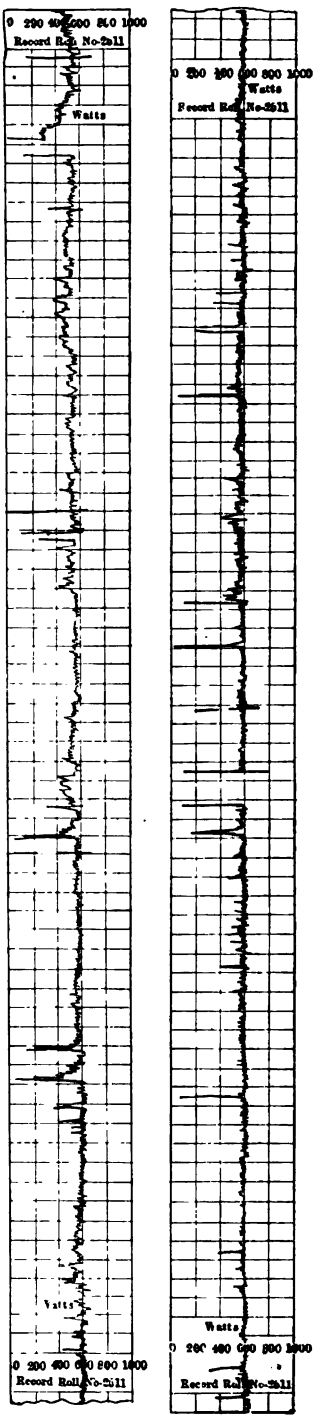

FIG. 14.—24-HR. LOAD CURVE OF FURNACE NO. 2. $K = 1.92$.

the percentage of time operated 90 to 95 per cent. The jump from a load factor of 79.9 per cent. in December to 85.1 per cent. in January, and the jump from 85.3 to 96.4 per cent. of time operated was due to the use of 24-in. electrodes instead of the smaller sizes, and better mechanical arrangements for changing electrodes on furnace No. 2.

The electrode consumption for the last four months of operation averaged 187 lb. (84.8 kg.) per gross ton of ferromanganese, or 162 lb. per short ton, or 32 lb. (14.5 kg.) per 1000 kw.-hr. passing through the electrodes. During this time 14-in., 17-in. and 24-in. electrodes were used. Except when using 24-in. electrodes, there was always one 14-in. electrode in the furnace but never more than one. About one half of the 17-in. electrodes were home-made "butt" electrodes produced at the plant from crushed broken electrode. These electrodes had 6 to 8 hr. greater life than the best purchased electrodes. This was because the

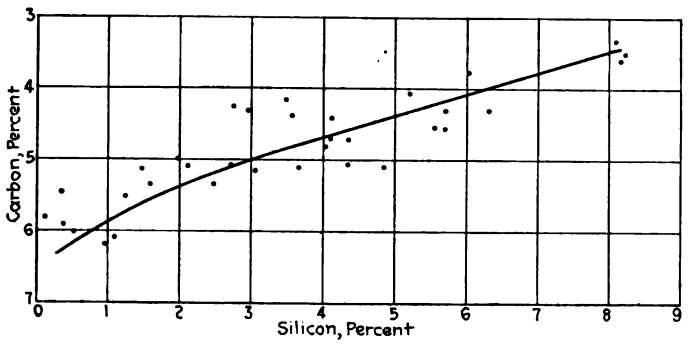

FIG. 15.—EFFECT OF VARIATION OF SILICON ON CARBON IN FERROMANGANESE.

material from which they were made was better material for electrode manufacture than that used in the purchased electrodes. It was more highly graphitized because it had been electrically calcined twice.

The beneficial effect of operating a furnace with the electrodes carrying their normal load or less is shown by the results of the January operation of furnace No. 2 with 24-in. electrodes. The electrode consumption for January averaged 141 lb. (63.9 kg.) per gross ton of ferromanganese, or 125 lb. per short ton, or 26 lb. (11.8 kg.) per 1000 kw.-hr. These electrodes were oversize for the load carried. A threaded electrode should not be operated with a load of over 30 amp. per sq. in. of cross-section, although a "butt" electrode will carry 50 amp. per sq. in. If threaded electrodes are overloaded, there is not only an excessive electrode consumption, due to the joint corroding and finally breaking, but much operating time is lost. With the 24-in. electrodes, no part of the electrode was lost except the connecting pin, which would drop out, but with the 17-in. threaded electrode it was common to lose 2 ft. of the electrode. It was as economical to use 17-in. butt electrodes as threaded 17-in. electrodes.

The average load carried by these electrodes was 10,500 amp. On this basis the electrodes were loaded as shown in Table 8.

TABLE 8.—*Current Carried by Electrodes*

Diameter of Electrode, Inches	Cross-section Area, Square Inches	Approximate Load, Amperes	Amperes per Square Inch
8 (four per holder)	201	10,500	52.2
14	154	10,500	68.1
16	201	10,500	52.2
17	227	10,500	46.3
24	452	10,500	23.2

TABLE 9.—*Analysis of Materials Charged and Tapped in Last Quarter of* 1918

	Manganese Ore, Dry, Per Cent.	Lignite Coal, Per Cent.	Limestone, Per Cent.	Lime, Per Cent.	Steel Turnings, Per Cent.	Ferromanganese, Per Cent.	Slag, Per Cent.
Manganese	34.8				0.81	73.6	12.4
SiO_2	13.2		1.5	1.1			28.6
MgO	0.4		0.15	0.7			2.4
Iron	7.1				97.85		
CaO	5.7		54.03	89.0			37.8
Al_2O_3	3.0						7.9
Phosphorus	0.038			0.072	0.052	0.10	
Sulfur	0.61			0.41	0.013	0.011	
BaO	2.3						
Moisture		13.84					
Ash		4.90					
Volatile matter		36.42					
Fixed carbon		44.84					
CO_2	7.09		42.3				
CO_2 and H_2O				8.7			
Copper					0.21		
Carbon					1.1		
Silicon					0.12	2.9	

TABLE 10.—*Summary of Operating Results in Last Quarter of* 1918

Manganese ore, pound	2,593,290
Coal, lignite, pound	1,125,000
Limestone, pound	421,477
Lime, burnt, pound	90,320
Steel turnings, pound	400
Ferromanganese, pound	887,312
Ferromanganese, gross tons	396.2
Slag, pound	1,122,741
Ratio ore to metal	2.92
Slag per gross ton metal, pound	2830
Slag per net ton metal, pound	2530
Total manganese in metal, per cent	72.0
Total manganese in slag, per cent	15.0

TABLE 10.—*Summary of Operating Results in Last Quarter of* 1918 (*Continued*)

Total manganese unaccounted, per cent	13.0
Electrodes, pound	80,047
Electrodes per gross ton metal, pound	202
Electrodes per net ton metal, pound	181
Electrode per 1000 kw-hr., pound	40
Tapping steel, pound	8,519
Tapping steel per gross ton metal, pound	21.5
Oxygen, cubic feet	400
Oxygen per gross ton metal, cubic feet	1.0
Fireclay, pound	33,858
Fireclay per gross ton metal, pound	85.5
Average maximum demand of plant[a]	1139.1
Total kilowatt-hours consumed in plant[a]	2,007,200
Average of plant, load factor per cent	80.5
Average time operated, per cent	86.7
Furnace days operated	79.7
Metal per calendar day, pound	9,664
Metal per furnace day, pound	11,133
Kilowatt-hours per gross ton metal, plant	5,066
Kilowatt-hours per short ton metal, plant	4,524
Kilowatt-hours per gross ton metal, furnace only	4,990
Kilowatt-hours per short ton metal, furnace only	4,457

[a] Includes approximately 30,000 kw.-hr. consumed in general plant operation.

Impurities in Ferromanganese

Elimination of impurities is not one of the problems of ferromanganese manufacture. As 0.2 per cent. phosphorus is allowable in ferromanganese, it is possible to use almost any ore by mixing it with a low-phosphorus ore. Sulfur is readily eliminated by the strong reducing atmosphere of the furnace, the basic slag, and the action of manganese carrying sulfur into the slag as manganese sulfide. Most of the sulfur that appears in analyses is probably from particles of slag in the sample. No attention is paid to the carbon content of the metal, because a low carbon alloy is seldom required. It fluctuates as shown in Table 11, decreasing with increased silicon in the metal.

Several electric-furnace plants make it a practice to produce ferromanganese containing 5 per cent. silicon, claiming that this is economical because it reduces the manganese loss by reduction of slag volume; the authors, though, cannot see the economy of producing metal containing over 2 to 3 per cent. silicon.

A series of tests made during plant operation showed that 1.15 per cent. of the sulfur charged remained in the ferromanganese. Of the 98.85 per cent. eliminated, 39.35 per cent. passed into the slag, and 59.5 per cent. was lost in dust or volatilized. Of the phosphorus charged 52.6

per cent. remained in the metal. Of the 47.4 per cent. eliminated, 20.81 per cent. was in the slag and 26.59 per cent. was lost in dust or volatilized.

TABLE 11.—*Effect of Increase of Silicon on Percentage Carbon in Ferromanganese*

Silicon, Per Cent.	Carbon, Per Cent.	Manganese, Per Cent.	Silicon, Per Cent.	Carbon, Per Cent.	Manganese, Per Cent.
0.12	5.79	80.65	3.47	4.15	78.57
0.30	5.89	77.62	3.55	4.37	78.56
0.34	5.45	82.86	3.66	5.08	74.7
0.37	5.90	81.4	4.01	4.80	78.84
0.52	6.01	83.89	4.09	4.69	79.92
0.98	6.17	79.21	4.11	4.42	80.19
1.10	6.06	80.55	4.32	5.02	77.75
1.24	5.52	79.84	4.33	4.69	77.16
1.48	5.12	82.65	4.84	5.18	78.97
1.50	5.78	81.4	5.17	4.04	78.28
1.57	5.35	79.15	5.56	4.53	78.16
1.97	4.97	79.4	5.63	4.54	79.15
2.10	5.07	79.65	5.68	4.30	75.18
2.48	5.35	81.77	6.06	3.76	76.53
2.70	5.07	79.85	6.32	4.31	75.31
2.72	4.25	79.46	8.07	3.28	73.44
2.95	4.30	79.79	8.16	3.60	75.64
3.05	5.13	79.52	8.22	3.49	75.20

COST OF MANUFACTURE OF FERROMANGANESE IN THE ELECTRIC FURNACE

It is possible to give the complete cost data of the plant described as the operating corporation has gone out of business. These costs are wartime costs. Table 12 shows the unit costs for the last four months of operation, and Table 13 the cost per gross ton of ferromanganese produced during this period. The labor employed was as follows:

	PER SHIFT	PER DAY
Master mechanic		1
Blacksmith		1
Unloading foreman		1
Unloading labor		2
Truck driver		1
Night foreman		1
Furnace foremen	1	3
Head charger and tapper	1	3
Furnace labor	3	9
Total	5	22

TABLE 12.—*Unit Costs*

	October, 1918, Cents	November, 1918, Cents	December, 1918, Cents	January, 1919, Cents
Manganese ore, high-grade, per pound.	1.77	1.54	1.51	1.41
Manganese ore, Leadville, per pound..	0.634	0.80	0.52	0.69
Lignite coal, per pound.....	0.242	0.235	0.23	0.25
Burnt lime, per pound.....	0.734	0.65		
Limestone, per pound.....	0.137	0.13	0.17	0.15
Carbon electrodes, per pound.....	10.00	11.6	9.70	8.78
Power, per kw.-hr.....	0.445	0.49	0.48	0.433
Tapping steel, per pound.....	5.34	6.57	6.04	5.36
Fireclay, per pound.....	0.45	0.50	0.45	0.45
Steel turnings, per pound.....			0.75	
Anthracite coal, per pound.....	.....			0.34

TABLE 13.—*Cost Per Gross Ton of Ferromanganese*

	October, 1918	November, 1918	December, 1918	January, 1919	Average per Month
Manganese ore.....	$76.44	$75.04	$77.49	$76.22	$76.29
Coal.....	7.15	5.93	7.16	6.25	6.62
Limestone and lime.....	2.47	4.58	2.26	3.14	3.11
Carbon electrodes.....	19.24	20.95	22.20	11.74	18.53
Tapping steel.....	0.73	2.39	0.97	0.49	1.15
Fireclay.....	0.40	0.50	0.32	0.30	0.38
Steel turnings.....			0.02		
Miscellaneous supplies.....	0.08	0.76	1.21		0.51
Power.....	22.65	23.35	25.30	23.44	23.68
Labor.....	20.12	21.65	23.24	21.51	21.63
Supervision.....	4.52	8.14	10.62	9.20	8.12
Repairs and renewals, supplies.....	1.77	2.32	1.83	1.07	1.75
Repairs and renewals, labor	1.92	1.99	1.84	2.11	1.96
Truck supplies.....	0.37	0.31	0.48	0.52	0.42
Truck, labor.....	0.67	0.70	1.19	0.92	0.87
Laboratory, supplies.....	1.56	0.46		0.09	0.53
Laboratory, labor.....	1.95	3.16	3.30	3.04	2.86
Administration.....	6.64	9.96	11.19	4.24	8.00
	$168.68	$182.19	$190.52	$164 28	$176.41

SUMMARY

The manufacture of ferromanganese in the electric furnace was the result of war demand for ferromanganese and the need of treatment of domestic ore in order to make available for war use a considerable tonnage of shipping used for transporting ore from South America. The industry

reached its peak in 1918, with a yearly production of 23,000 tons valued at about $5,000,000, or 7 per cent. of the total ferromanganese production of the United States. During 1919, there was little electric furnace production, but operations were resumed early in 1920, with an estimated production for the year of 10,000 tons. Nine plants in this country have produced ferromanganese in the electric furnace, all but one of which were constructed for that purpose. There are installed 33 electric furnaces of from 350 kv-a. to 5000 kv-a. capacity, with a total installed transformer capacity of 58,000 kv-a. The future of the process rests in its use as a method of ore treatment by the owner of a manganese mine with other favorable local conditions.

Comparing blast-furnace production of ferromanganese with electric-furnace production the paper shows that the same recovery of manganese, 72 per cent., was made in the electric furnace smelting of ore containing 34.8 per cent. manganese and 13.2 per cent. SiO_2, as in the blast furnace smelting of ore containing 40.33 per cent. manganese and 8.6 per cent. SiO_2. The slag and stack losses were practically the same in each case. The electric furnace consumes approximately one quarter of the quantity of carbon required by the blast furnace. It is probable that on the same grade of ore, the electric furnace would show at least 5 per cent. greater recovery than the blast furnace.

In smelting oxide ore, better operating results were obtained when any necessary iron was added in the form of manganiferous ore rather than as steel turnings. There was no economy in the use of lime as a flux instead of limestone. Lignite coal proved to be a better reducing agent than anthracite, bituminous coal, or coke, although coke was not given a long trial. From the viewpoint of output, power consumption, and labor costs, intermittent charging gave better results than continuous charging. Good results were obtained by tapping into cast-iron pots instead of beds.

Some of the operating difficulties that may be encountered are: formation of carbide in the furnace, blowing, failure of bottom, tapping, failure of electrode holders, and bridging of charge. Of these troubles formation of carbide is the most serious. The tendency to form carbide can be decreased by the use of lignite coal as a reducing agent; by not attempting to produce a slag containing much less than 12 per cent. manganese; and by the use of a low-carbon flushing charge when carbide begins to form. Blowing is decreased by intermittent charging, and by elimination of fine material in the charge. The authors prefer the magnesite bottom to the carbon bottom. Failure of electrode holders is a matter of design. Bridging of the charge is eliminated by proper spacing of electrodes.

Manufacture of ferromanganese containing 73.6 per cent. manganese was accomplished in an 1100-kw. electric furnace by smelting ore con-

taining 34.8 per cent. manganese and 13.2 per cent. SiO_2 with an average power consumption of 4990 kw.-hr. per gross ton, or 4457 kw.-hr. per short ton. There was tapped 2830 lb. (1283.7 kg.) of slag per gross ton of ferromanganese. The electrode consumption averaged 202 lb. per gross ton of metal, but during the last month of operation averaged 141 lb. per gross ton, or 125 lb. (56.7 kg.) per short ton, or 26 lb. per 1000 kw.-hr., which is what can be attained regularly. The plant operated 89.1 per cent. of the total time during the last four months with an electrical load factor of 81.6 per cent. using hand regulation of electrodes. The load factor for the last month was 85.1 per cent., and the percentage of total time operated was 96.4 per cent., figures which can be made regularly by experienced operators.

The average cost of production, f.o.b. plant, exclusive of taxes, interest, depreciation, and sales expense, during the period of four months when materials on hand permitted continuous operation of one 1100-kw. furnace was $176.41 per gross ton. Excluding reduction of costs due to cheaper ore supply, cheaper power, better design of plant, and higher operating efficiency, considerable reductions in cost of production of ferromanganese in the electric furnace are possible if the Soderburg continuous feeding electrode now installed in one plant continues to be a success, and if the unaccounted loss of manganese can be decreased.

DISCUSSION

A. L. STILLMAN, New York, N. Y.—The paper states that some blowing and trouble was due to fine material; was any attempt made to briquette this fine material?

ROBERT M. KEENEY.—During the last month of the operation we mixed the charge with the lime, let it set with water, and then shoveled it into the furnace; the results were quite satisfactory so far as dust loss was concerned.

J. W. RICHARDS,* South Bethlehem, Pa.—I have made a rather careful study of why the manganese goes into the slag. Increasing the lime increases the difficulty of the production of carbide, as Mr. Keeney has brought out, but apparently increasing alumina may also decrease the amount of manganese in the slag. The slag with the lowest percentage of manganese has the highest percentage of alumina, so that alumina may satisfy the silica and reduce the amount of manganese in the slag without the formation of so much calcium carbide. It might be, therefore, possible to use some manganese ore high in alumina to increase the alumina in the slag and thus decrease the amount of manganese.

* Professor of Metallurgy, Lehigh University.

The volatilization losses mentioned are important and somewhat mysterious because they are not apparently all accounted for by the dust. People that work with these ferromanganese furnaces suspect that some volatile manganese compounds pass out of the furnace. Manganese carbonyl has been mentioned as one possible source for the escape of the manganese, and it is not outside the realm of possibility that some such volatile manganese compounds are formed which increase the losses. A study of these compounds, the conditions of their formation and their decomposition and their relation to the operation of the furnace, might lower the volatilization loss.

The Soderberg electrode, which was first used in America on a ferromanganese furnace, may reduce the electrode costs of the operation at least 50 per cent. The electrode consists of an iron casing into which is placed the soft carbon mixture of which electrodes are ordinarily made. Ribs inside the casing hold the soft mix in place. A well-designed holder, with water-cooled plates, fits on the outside of this casing just above the level of the charge. After the casing filled with soft mix is put in place, the furnace is started. A fire is made in the furnace until the electrode is slowly baked up to and above the electrode holder. Then current is put on. The heat which is transmitted upward from the furnace then bakes the electrode as it descends, so that there is, in general, about the same amount of baked electrode in operation all the time and the upper part is always soft. As the electrode is consumed, the whole electrode is dropped by loosening the screws on the holder and letting the electrode drop down.

When enough of the electrode has been consumed, another section of casing is electrically welded to the upper end, the men standing upon a platform built above the furnace. This section is then filled with the soft mixture. A ferromanganese or ferrosilicon furnace may need a 3-ft. section a week. In Norway, one 34-in. electrode was used continuously for a year; it will last as long as the furnace lasts.

Practically no hydrocarbons are given out during the operation of the furnace. I expected to see a lot of yellow smoke from the baking of the carbon; but the upper part of the electrode is packed so tight that the hydrocarbons cannot escape. They must go down into the furnace, and as they pass over the white-hot part of the carbon, they are decomposed and deposit carbon, strengthening the electrode by so doing. A furnace at Anniston, Ala., has three 32-in. electrodes; a furnace in Norway has a 34-in. electrode, and a furnace operating on calcium carbide in Africa has a 37-in. electrode.

I see no reason why the electrodes cannot be made just as large as desired. The total cost at the most is one-half that of the ordinary electrode, even including the royalties, because less carbon is used. It is my opinion that this electrode will displace about three-quarters of the large furnace electrodes now made.

W. N. CRAFTS, Montreal, Que.—What is the current density capacity of this electrode?

J. W. RICHARDS.—The electrodes were designed with exactly the same cross section as those previously used, and they carry the same current density quite easily. I believe they could be speeded up 100 per cent. The iron casing practically carries all the current down to the part that is hard baked. The upper end of the electrode is non-conducting; it is so soft that a rod can be pushed right through it.

W. N. CRAFTS.—Have these electrodes been applied to tilting furnaces?

J. W. RICHARDS.—Yes, at the Stavenger Steel Company's works in Norway. There, however, the used electrode is replaced by another. This work, though, does not take more than 10 min. I have seen them in 3 min., loosen the screws, slip the electrode down 9 in., and then screw it tight again without taking off the current.

W. N. CRAFTS.—What thickness of metal is used?

J. W. RICHARDS.—About $\frac{1}{16}$ in.

D. A. LYON, Washington, D. C.—That electrode could not be used on a cold-top furnace. Many people, I think, have a wrong idea about this casing; they think it must be heavier than it is. The furnace at Anniston, with which they are making ferrophosphorus, is operating as nicely as any furnace I ever saw. They have a ferrophosphorus furnace making phosphoric acid, but the Söderberg electrode is not used on that. There are not many hydrocarbons coming off; but at Anniston they prepare the mixture and tamp it in the casing in a room built just above the cables. Before the workmen go in, however, they turn on the fan for about 4 or 5 min.

J. W. RICHARDS.—That booth is made out of reinforced cement, the cement floor having water cooling pipes. The electrode passes through a stuffingbox so that the floor is perfectly gas tight. The first time I saw one of those furnaces I remained in that room for nearly an hour; the air was better there than on the furnace floor around the furnace. But that permanent platform or room cannot be used on a tilting furnace.

E. S. BARDWELL,* Great Falls, Mont. (written discussion).—On page 557, two formulas are given showing the reduction of manganese carbonate by carbon. These formulas are misleading, as any $MnCO_3$ charged to the furnace is calcined before it reaches a zone in the furnace

* Metallurgist, Great Falls Reduction Dept., Anaconda Copper Mining Co.

where the temperature is sufficiently high to permit reduction to take place. The following formulas would better represent furnace conditions:

$$MnCO_3 + \text{heat} = MnO + CO_2$$
$$MnO + C = Mn + CO$$

I can see no reason for introducing silica into the reaction. Most of the furnace accretions that I have examined have consisted of a mixture of carbide and graphite. While very likely silica is present in the form indicated by the authors, it is not required to bring about the formation of carbide. An excess of carbon not only promotes the formation of carbide but causes loss of manganese, not so much from lack of lime to combine with the silica as from lack of carbon to reduce the manganese. Every molecule of carbide formed removes two atoms of carbon for every atom of calcium combined to form carbide; in addition, one more atom of carbon has been used in effecting the reduction. The manganese is not carried into the slag as a silicate but, owing to failure to be completely reduced, may form manganates or maganites of the bases present and so pass into the slag. Manganese silicate rarely exists, to any considerable extent, in electric-furnace slags and when it does the slags are pink. I have only once seen such a slag from the electric furnace. Formation of carbide may be promoted by improper mixing of the charge or by improper sizing of the constituent particles to such an extent that the charge becomes stratified in the furnace.

In the two installations described, the reactance of the transformers in one case is 10 per cent. and in the other 7 per cent. Why should every attempt have been made to minimize reactance between the transformer and furnace and a transformer of such high reactance be employed? I am familiar with several installations in which the transformer reactance is not over 4 per cent. and know that no difficulty has resulted therefrom.

For ferromanganese, magnesite bottoms are likely to be perfectly satisfactory when properly installed and with sufficient provision for air-cooling. Carbon bottoms are cheaper in first cost and, if properly installed, stand up well.

The authors have well stated the situation with reference to reducing agents. In one plant coke braize has been successfully used. If free from dust, no more need be used than is necessary to supply carbon to reduce the manganese and iron, if iron ore is used, and supply the carbon required by the metal.

The authors state that continuous charging may result in greater tendency to formation of carbide than intermittent charging. This is not so much a question of the manner of charging as it is of what takes place after charging. If a charge is so made up that as it sinks in the furnace there is a tendency to stratify, intermittent charging would

probably help, but why not use a charge that once mixed will stay mixed?

After experimenting with casting in sand pits, tapping in ladles, and casting in machines after skimming slag, I agree with the authors that the most economical method for handling metal from the furnace is to tap into pots. But an iron similar to that employed for steel ingot molds should be specified—low phosphorus and with at least 2 per cent. silicon. Such pots should be able to stand more punishment and give greater service than ordinary mixtures.

With higher voltage wider spacing of the electrodes is permissible. In a furnace that is operating nicely, the charge should sink down fairly uniformly after each tap. A tendency to form bridges between the electrodes reduces the smelting capacity of the furnace and is to be avoided.

The power factor is given as between 85 and 90 per cent. The power factor for the maximum load in these furnaces depends largely on the frequency. With a 60-cycle furnace current, the power factor at maximum load would be approximately 71 per cent.; with a 25-cycle current, the furnace would have better than 93 per cent. power factor at maximum load. Where a high-power factor is desirable, there would be a distinct advantage in operating on 25-cycle rather than 60-cycle current. The power factor given merely shows that the furnace was not carrying maximum load possible at the voltage at which it was being operated.

After studying a number of furnaces operating at different voltages and using electrodes of various sizes, I am inclined to proportion the electrodes on the basis of energy density rather than current density. Better results will be obtained if the total cross-sectional area of electrodes is such that there is 1 sq. in. of cross-sectional area for every 0.75 kw. input. This figure is only approximate and would call for one 24-in. round electrode on each phase for an 1100-kw. furnace and for a 1600-kw. furnace the equivalent of one 30-in. round electrode per phase.

In the comparison between the electric furnace and the blast furnace, the authors have understated rather than overstated the case. One plant at least has operated furnaces up to 1600 kw. capacity with recoveries of between 86 and 90 per cent. when working on ores of the same average quality that go to the blast furnace. Small furnaces of 1100 kw. input have consistently made 90 per cent. recoveries even on low grade ores.

Importance of Hardness of Blast-furnace Coke

By Owen R. Rice,* Ch. E., Bethlehem, Pa.

(New York Meeting, February, 1921)

Changes in coke hardness affect the working of the blast furnace, for soft coke is an obstacle to proper furnace operation. Soft coke is due to a low hydrogen-oxygen ratio in the coal charged; increasing this ratio increases the hardness of the coke. The best means of determining the hardness of coke is the combined tumbler and ball-mill.

What is Good Coke?

It is not always appreciated that the correct answer may be such a reliable forecast to the physical condition of the blast furnace, and incidentally its entire operation, that among the ordinary variations in other raw materials and also in operating conditions, it assumes a position of primary significance. Inasmuch as coke forms two-thirds of the total bulk of material charged, this assertion will not seem exaggerated, and in the subsequent discussion its applicability will be presented.

Coke is the ideal blast-furnace fuel because it is strong and hard enough to resist the crushing and grinding effects of the furnace burden, and its porosity allows the ready passage of gas upward through the charge, and rapid combustion before the tuyeres. Coke deprived of its strength and with a cell structure physically frail and chemically susceptible to solution by carbon dioxide has its chief asset eliminated. When the melting zones are approached the fluid cinder trickling toward the hearth will envelope the small pieces of coke and form a sticky mass that will retard the free passage of gas. Blast pressure will then rise, driving will slow up and fragments of coke will lie inert before the tuyeres, rendered practically incombustible by their slaggy envelop. It is believed also that coke messes at cast are attributable to quantities of such coke floating unburned in the hearth.

It has been correctly claimed that coke rendered small outside the oven possesses greater combustibility than that so developed in the

* Metallurgical Assistant, Blast-furnace Dept., Bethlehem Steel Co.

coking process. While this is true of reduction in size by ordinary breakage or shattering, where the porous inner cell structure is cleanly exposed, it does not hold true of coke that is ground small, for the grinding action causes the fine dust-like particles to enter the cells and so form a dense and quite incombustible surface.

Satisfactory Test for Hardness of Coke

The importance of initial size and the resistance of coke to reduction in size has been recognized, but methods thus far employed to determine the physical nature of coke have not given full satisfaction. The shatter test, now largely employed, usually consists in dropping 2-in. coke[1] four times upon an iron plate from a 6-ft. (1.8 m.) elevation and then screening through certain sizes of mesh, the various sizes thus separated being reported as percentages. This gives an indication of the condition of the coke when it reaches the furnace, having passed through the four major stages of handling; viz., cars to bins, bins to larry, larry to skip, and skip to bells.

But it must not be supposed that reduction in size ceases when the bells are lowered and the coke passes to the furnaces. It will continue and may even be accelerated throughout the entire passage from stock line to tuyeres. The gases will endeavor to disintegrate the cell structure and the mass of stock will exert a destructive grinding and crushing effect. Therefore, while a shatter test may indicate the extent of size reduction due to handling, it does not show the condition of the coke when it reaches its field of action—the tuyeres. Indeed there is frequently misguidance when the shatter test is depended on to determine fit or unfit—hard or soft—blast-furnace coke.

If a shatter test shows high fragmentation, the coke may have a weak, chalky structure that will resist no physical strain and cell walls susceptible to carbon-dioxide solution; or the coke may be glass-like in its brittleness but strong enough to bear the grinding, crushing, and abrasion of the brickwork, limestone, scrap iron, etc., on the way to the tuyeres, maintaining throughout a size that permits it to function properly as a porosity medium and that precludes the likelihood of its being "drowned" in slag. The coke that resists shattering is either the tough, soft variety, which is sure to yield to the abrasive action later on; or it is the strong, hard kind that is not susceptible to any sort of physical attack. The need for a more reliable test is, therefore, quite evident.

The effort to apply a test that more closely follows the treatment of coke in the furnace was stimulated by the article of G. D. Cochrane[2]

[1] By 2-in coke is meant that portion of the original sample that remains upon a 2-in. mesh.

[2] *Blast-furnace and Steel Plant* (Dec., 1918).

in which he compares the results of a tumbler test on coke with the operation of a low-pressure furnace. In following his lead, we have used a combination tumbler and ball-mill to determine the hardness of daily coke to three 500-ton furnaces, D, E, and F. The bosh angles of the furnaces are 76°, 76°, and 73½°, respectively.

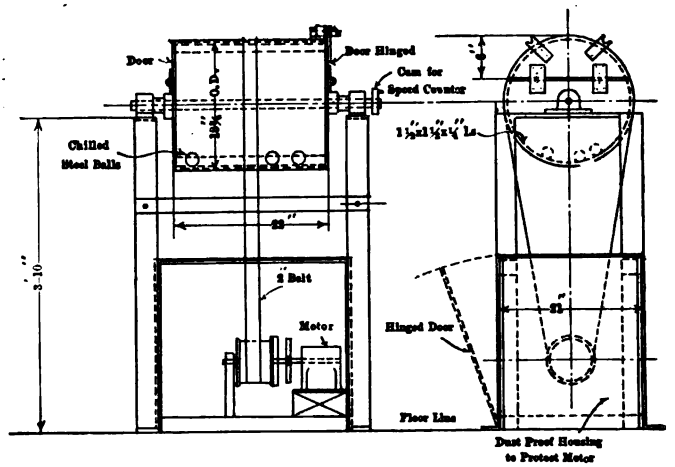

FIG. 1.—APPARATUS USED BY BETHLEHEM STEEL COMPANY TO DETERMINE HARDNESS OF COKE.

Our apparatus, shown in Fig. 1, is a 22-in. (56 cm.) steel drum, 18¾ in. in diameter with doors at either end and four 1½-in. angles riveted inside longitudinally. A ¼-hp. motor drives the drums at about 20 r.p.m., the belt passing from the motor gear train over the drum itself. Thirty pounds of dry 1-in. coke[3] about half fills the drum. This sample is tumbled for 1250 revolutions (at 20 r.p.m.) with eleven 1¼-in. (32 mm.) steel balls. The resulting fines are screened through ½-in. mesh, and the remaining portion is weighed and reported as per cent. of original. This quantity is termed the coke hardness number.

The results of the regular shatter test are shown in Fig. 2 as per cent. through 2-in. mesh, and after four 6-ft. drops upon an iron plate. The results of both the tumbler test and the regular shatter test were compared with furnace operation on each subsequent day when the coke tested was passing through the furnace. A period of two months was selected as typical of conditions at that time, being marked by irregularity both of raw materials and in furnace behavior. The hard ores, for example, varied in furnace D from 0 to 100 per cent.; in furnace E, from 0 to 20 per cent.; and in furnace F were fairly constant at 25 per cent. Tons of stone used per ton pig produced varied widely, the daily averages covering a range of 0.40 to 0.65 ton. The daily averages of scrap charged per

[3] By 1-in. coke is meant that which passes 2-in. and remains on 1-in. mesh.

ton pig produced ran from 0.08 to 0.35. Coke consumed per ton pig varied as much as 20 per cent. on each furnace. The operators fought the wide variations in blast pressures that were constantly threatening, and maintained an average pressure of 17 lb. (7.7 kg.) for the period.

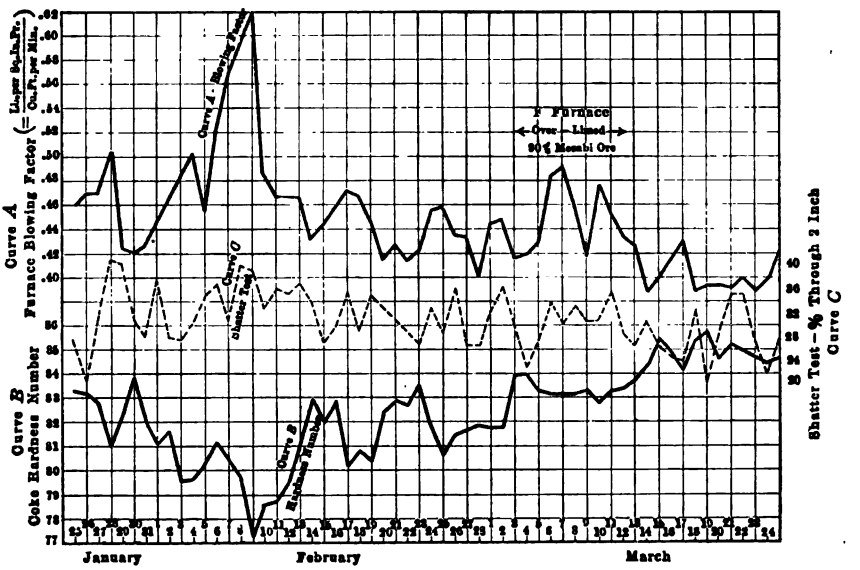

FIG. 2.—RELATION OF FURNACE OPERATION TO COKE HARDNESS.

The blowing factor is simply the ratio between the blast pressure and blast volume:

$$\text{Blowing factor} = \frac{\text{average blast pressure, lb. per sq. in.}}{\text{average wind blown, cu. ft. per min.}} \times 1000.$$

In no way is the physical well being of a furnace so truthfully indicated as by the blowing conditions. The blast is the pulse of the furnace. Pressure and volume conditions must be considered simultaneously, however, for the furnace may be driving well with pressures up to 18 or 20 lb. due merely to rapid blowing; or it may be hanging and slipping and may require slackening of the engines with but 14 or 15 lb. pressure. High pressure and low volume produce a high blowing factor and indicate poor working; low pressure and large volume yield a low blowing factor and show proper furnace conditions. As a matter of daily record, blowing conditions furnish more reliable data on the health of the furnace than either tonnage or rounds charged, both of which depend largely on the nature of the ores used or the size of burden; and both are affected by delays. Moreover, both tonnage and rounds charged, other conditions being constant, are direct consequents of blowing conditions.

The almost unfailing inverse coördination, day by day, between the hardness number and the blowing factor was enlightening, particularly in the face of the numerous operating irregularities that marked the test period. It was only between Mar. 5 and 10, when furnace F was carrying 80 per cent. of a Mesabi ore that has always caused trouble, that the furnace worked badly in spite of fairly hard coke. Hardness number was between 83 and 84 at the time. Cold stock reaching the hearth, due to heavy slips, led to off casts and large excess of stone was carried to curb the rising sulfur in the pig; this further aggravated high pressure

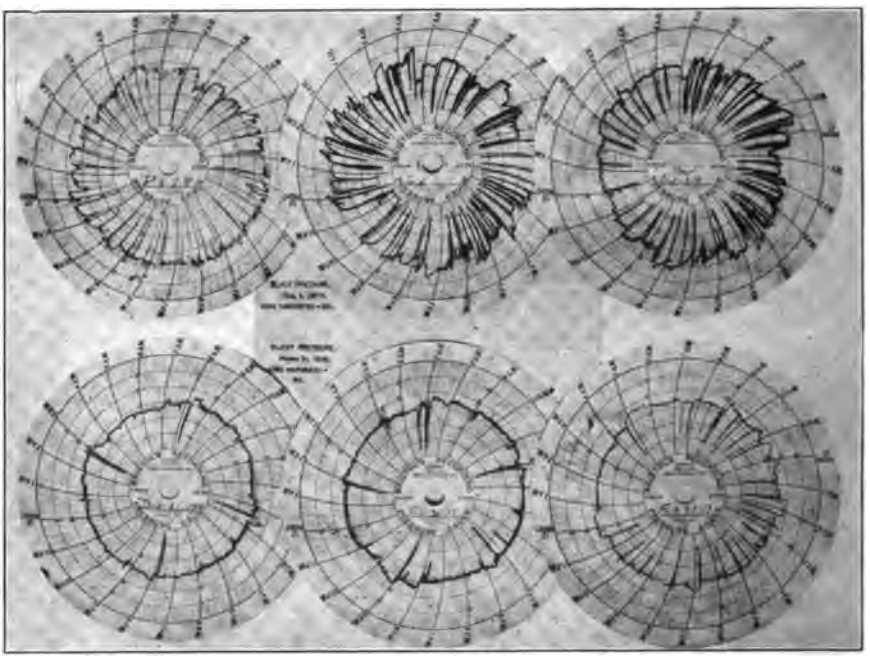

FIG. 3.—PRESSURE CHARTS SHOWING CONDITION OF FURNACES WITH SOFT COKE AND WITH HARD COKE.

conditions.

The two sets of pressure charts shown in Fig. 3 give evidence of the condition of the furnaces when working with the soft coke and with good, hard coke. The conditions on Feb. 7 and Mar. 21, as shown in Fig. 2, should also be compared.

It would be absurd to claim that hard coke alone is the remedy for all blast-furnace maladies, for furnace operation fluctuated when the coke hardness did not. But there was no material change in coke hardness that did not show its effect upon the furnaces. The curves in Fig. 2 are comparable day for day, the coke data having been advanced by one day.

What has been said concerning the shatter test must not be construed

as condemnatory of its general value. Fig. 4, showing the direct relation to furnace blowing factor of the shatter test and hardness number, respectively, demonstrates the coördination between furnace conditions and the quality of coke. That the furnace is more sensitive to change in the hardness of coke (tumbler test) than to change in the toughness of coke (shatter test) is shown by the daily comparison between hardness and furnace condition; see Fig. 2. For example, on Jan. 28, the shatter tests indicated the most brittle coke of the entire test period, 40 per cent. through 2-in. mesh, but the furnace operation was normal, as registered by a blowing factor of only 0.480. About Feb. 8, the shatter test again showed 40 per cent. through 2-in. mesh, but this time the furnaces were in poor condition; pressures were up to 25 lb. and the blowing factor

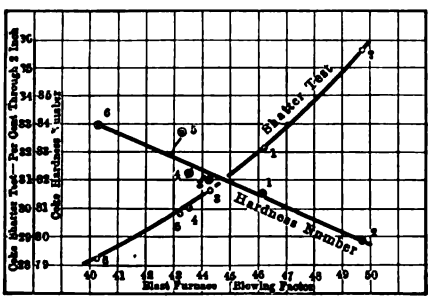

FIG. 4.

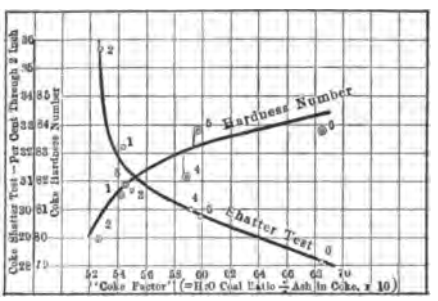

FIG. 5.

FIG. 4.—RELATION OF FURNACE CONDITION TO COKE HARDNESS SHOWN BY SHATTER TEST AND HARDNESS NUMBER.

FIG. 5.—EFFECT OF COAL HYDROGEN-OXYGEN RATIO AND COKE-ASH CONTENT ON COKE HARDNESS SHOWN BY SHATTER TEST AND HARDNESS NUMBER.

reached 0.620. The best furnace week was that of Mar. 21, when the blowing factor was steady at 0.400 for seven days, but the shatter test showed both unwarranted variation and magnitude, being as high as 35 per cent. through 2-in. In each instance the hardness number was in accord with the furnace operation.

Hard coke means satisfactory furnace operation. Below a hardness number of 81, the furnace showed very seriously the effect of soft coke. Hardness over 85 does not show any particular effect, good or otherwise, upon furnace conditions. Beyond a doubt what must be sought in the furnacing quality of coke is its resistance not only to fragmentation but to abrasion. This characteristic is well indicated by the tumbler test. The use of steel balls in the tumbler is advantageous, as in the furnace the coke is in contact with masses of greater density than itself. The introduction of hot carbon-dioxide gas would add both interest and complexity to further investigations.

The numerical value of the blowing factor is affected by the initial size of the coke. If more than 45 per cent. passes through a 2-in. mesh,

it requires little further reduction in size to tie up the furnace with a bad case of "small-coke indigestion." Hence if numerical comparison is sought between furnace behavior and the hardness of a coke that varies greatly in initial size, that item must be taken into consideration. During the test period, there was no marked variation in size.

Conditions Affecting Hardness of Coke

While the coal used is the most important factor in determining coke quality, it is difficult to establish a rule governing the quality of coke resulting from different coals, particularly those recognized as coking coals. We have verified the theory of David White[4] that the hydrogen to oxygen ratio on a dry-coal basis affects the resulting coke quality, even substituting for quality the unpretentious term hardness, and though limited to but 20 points variation in the ratio (72 to 92 per cent.) as compared with his range of 10 to 290 per cent. Average values for successive 10-day periods show rather steady increase in both hydrogen-oxygen ratio for the coal used, and the hardness of the coke produced.

Period	Average Hardness Number of Coke	Shatter Test Per Cent. Through 2 In.	Hydrogen-oxygen Ratio of Coal	Per Cent. Ash in Coke
Jan. 25 to Feb. 3	81.65	32.30	73.20	13.47
Feb. 4 to Feb. 13	80.00	35.74	72.00	13.67
Feb. 14 to Feb. 23	82.00	30.96	74.90	13.70
Feb. 24 to Mar. 5	82.39	30.16	81.00	13.64
Mar. 6 to Mar. 15	83.77	29.92	81.60	13.62
Mar. 16 to Mar. 24	83.91	28.30	91.20	13.27

Doctor Cochrane[5] has shown the detrimental effect of ash in coke upon its hardness. The variation of ash in our coke, though small, was sufficient to corroborate Cochrane's claim, and ash content has been considered in this investigation as second among conditions that influence quality.

The third and final consideration is that of oven practice, as represented by the heat applied in coking. As heat is maintained in the empty ovens during slack times and as 75 per cent. of the coke was pushed on day shift, with an average coking time of 33 hr., some of the coke was short-period coke, and some long-period coke. The reported heats, in British thermal units per pound coal charged, are not deemed sufficiently accurate for purposes of direct comparison throughout the test period. We are satisfied, however, that overcoking has a detrimental effect on hardness; that while overcoking increases the depth of dense surface, it weakens the cell walls and structure, rendering the coke susceptible to attrition. The unprecedented drop in coke hardness from Feb. 5 to

[4] David White: Bureau of Mines *Bull.* 29.

[5] *Op. cit.*

10 is attributable largely to overcoking, there being an increase from about 1250 B.t.u. per pound coal during the previous 10 days, up to about 1500 B.t.u. during the period Feb. 5 to 10. The coal used during this period exhibits no great variation over that charged immediately previous or subsequent thereto. The hydrogen-oxygen ratio was low (72 per cent.) but nearly constant. During the final 10-day period of the test, the number of British thermal units per pound coal again rose to about 1500, and served to counteract the effect of the high hydrogen-oxygen ratio, at this time about 90 per cent., in raising the coke hardness. No data are as yet available on the hardness of green coke, but it is reasonable to believe that such coke will be soft. In undercoking, strong cells walls have not yet been established; in overcoking, the cells have been enfeebled. Comparisons have been drawn between the hydrogen-oxygen ratio in coal and ash in coke, on one hand, and the hardness of coke on the other, averages being taken over successive 10-day periods. The hydrogen-oxygen ratio and ash have been incorporated into a factor:

$$\frac{\text{hydrogen-oxygen ratio}}{\text{per cent. ash in coke}} \times 10 = \text{coke factor}$$

which is plotted against both tumbler and shatter tests, in Fig. 5.

With fairly uniform coke ash, as the hydrogen-oxygen ratio drops below 74 per cent., the hardness of the resulting coke falls off rapidly; as the ratio exceeds 87 per cent., the effect on coke hardness becomes less and less marked.

That stocking coal affects the hydrogen-oxygen ratio is shown by the following: A 9-mo. stock of Davis coal showed a ratio of 102 per cent., while Davis coal direct from the mine showed a ratio of 125.8 per cent. Some 9-mo. stock of Fulton coal showed a ratio of 55.1 per cent. while Fulton coal direct from the mine showed a ratio of 57.5 per cent. It was the steady increase in the use of fresh coal that brought about the regular rise of the hydrogen-oxygen ratio throughout the test period.

Summary

Coke hardness has an extremely marked effect upon blast-furnace health.

The furnace is more immediately sensitive to hardness, which resists wear and tear within the furnace, as shown by the tumbler test, than to toughness, which resists rough handling without the furnace, as shown by the shatter test. The tumbler test is therefore superior for daily control; its adoption is also recommended on grounds of simplicity, reduction of the personal equation, and the saving of labor.

The shatter test is of value as a matter of general record but does not surpass the tumbler test in this respect.

Both tests for coke hardness show reliable coördination with the hydrogen-oxygen ratio of the coal used; the higher this ratio, the harder the coke.

DISCUSSION

OWEN R. RICE.—While determining the furnaceability of coke it is important to bear in mind the fact that combustibility plays a considerable part in blast-furnace working.

C. R. MEISSNER, Pittsburgh, Pa.—This test is a step in the right direction and will show good comparative results for a given coke at a given furnace; but a person must be careful about saying that the harder the coke the better for any furnace plant. Coke made from 80 per cent. Pittsburgh coal and 20 per cent. Somerset coal is a very hard strong coke, but it is quite dense and in large pieces. In a blast furnace, like some eastern Pennsylvania furnaces, making about 200 tons per day, this coke did not give good operation. The blast pressure dropped, the furnace was hot on top, and it made high-sulfur iron. With coke from 100 per cent. Pittsburgh coal, the same furnace made good low-sulfur iron and the top was cool. That straight high-volatile-coal coke would have shown less hardness in the tumbler barrel than the 80-20 mixture; but for that furnace it was better because it was more combustible.

The coke is rather friable at Bethlehem; the stronger they get it the nearer it comes to being right for their big furnaces. At a plant like the Jones & Laughlin Co., in Pittsburgh, the same thing might be true; a little stronger coke would be better for their furnaces. On the other hand, for the smaller furnaces or where the coke conditions are such that the coke tends to be stronger and harder anyhow, there is a possibility of getting it too strong. So the test should be judged on the basis of the coals used and the furnaces using them. How was the coke sample used for the test taken? Through what mesh was the 30-lb. sample screened?

OWEN R. RICE.—The coke sample is always taken from the car. A bucket about 1 ft. deep and 1 ft. in diameter is clamped on the rail below the hopper; then when the car is opened, a lid on the bucket is slowly drawn open with a rope. The operator stands some distance away. He tries to get a representative sample through the depth of the car.

The 30-lb. sample was made up of material that passed through a 2-in. mesh and remained on 1-in. mesh.

J. W. RICHARDS,* South Bethlehem, Pa.—Blast-furnace managers speak in general of the combustibility of the fuel as merely a qualitative term; we need quantitative data by which we can say that coke made at a

certain temperature has a certain solubility in carbonic acid, so that we know exactly how quickly it acts upon the carbonic acid to reduce it in the furnace. The term "solubility of coke in the upper part of the furnace" has always struck me as being exceedingly indefinite and unsatisfactory and should be made precise.

RICHARD MOLDENKE, Watchung, N. J.—The testing of coke for its ability to carry a burden can be somewhat simpler for foundry purposes than in the case of the blast furnace, as the column to be supported is seldom over 25 ft. high. The reason for such a short height, as compared with the great heights in a blast furnace, is that within the 15 to 25 ft. charged in a cupola there is enough metal to absorb sufficient heat from the waste gases to allow the escape of only sufficient heat up the stack to give the proper draft. The test described for coke is a very good one not only for blast-furnace purposes but also for foundry coke. I would recommend, however, that the quantities used be larger, necessitating a tumbling barrel of larger capacity.

R. S. REED, Ashland, Ky.—Is a 30-lb. sample adequate for all classes of work? Some put the standard as high as 1500 pounds.

OWEN R. RICE.—The larger the sample is the better; we use a 50-lb. sample for the shatter test and about 250 lb. for the screen test. We take a bucket full from each car and the moisture sample is run on a higher amount. The coke is placed in pans about 2 ft. long and 8 in. wide. Then one pan out of every three is selected for the screen test.

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* Professor of Metallurgy, Lehigh University.

Blast-furnace Flue Dust

By R. W. H. Atcherson,* Indiana Harbor, Ind.

(New York Meeting, February, 1920)

Blast-furnace flue dust is one of the most troublesome operating factors in the iron and steel industry. It is usually involved in all the unpleasant phases of blast-furnace operations. It adds to our aggravations until we are willing to spend large sums of money to keep it out of our stoves and boilers and more money to handle it again and again on one scheme or another to induce the furnaces to retain it without bad after effects.

Several successful operators claim that it is useless to recharge raw flue dust because the furnace would never have blown it out if it had been suitable material for blast-furnace consumption. Most of us who have made persistent efforts to return raw flue dust to the furnaces have decided that it is very often false economy to do so. Yet some remarkable results have been attained at the Ohio Works of the Carnegie Steel Co. through recharging raw dust. The plant comprises six modern blast furnaces. Up to 1909, about 300,000 tons of flue dust had accumulated in stock piles. During the last 10 years, there have been recharged into these furnaces all of the flue dust recovered from the furnace operations, the entire stock pile of flue dust, and nearly 80,000 tons of dust shipped from other furnaces of the Carnegie Steel Co. The results obtained are shown in Table 1.

Table 1.—*Blast-furnace Practice, Years* 1909 *to* 1919

Year	Total Ore Consumed, Tons	Per Cent., Mesab Ore	Tons Flue Dust Used	Tons Flue Dust Produced	Pounds Coke per Ton Iron	Iron Produced, Tons	Actual Yield, Per Cent.	Theoretical Yield, Per Cent.	Per Cent. Furnace Loss or Gain
1909									
1910	4,157,485	83.61	457,103	198,544	2,101	2,420,815	57.23	54.99	Gain 2.24
1911									
1912	1,790,822	84.94	111,184	88,466	2,206	978,604	53.78	54.33	Loss 0.55
1913	1,606,026	82.80	90,370	100,371	2,340	862,962	52.88	54.54	Loss 1.66
1914	1,149,869	82.87	111,691	60,959	2,091	655,596	55.60	55.21	Gain 0.39
1915	1,955,195	80.29	111,322	81,079	2,085	1,090,579	54.39	54.54	Loss 0.15
1916	2,027,792	85.65	118,980	96,630	2,075	1,134,429	54.72	54.78	Loss 0.06
1917	1,769,028	86.22	112,985	102,791	2,143	994,822	54.65	55.53	Loss 0.88
1918	1,720,585	92.36	94,852	102,335	2,210	950,076	54.43	55.10	Loss 0.67

* Blast-furnace Superintendent, Inland Steel Co.

In common with a great many blast-furnace men, we have tried many schemes for reducing the amount of dust carried out by the gas and numerous ways of recharging it, in both the raw and the sintered state. We have operated on inconsiderable percentages of Mesabi ore and again have used nothing but Mesabi for years at a time. Yet we are still making a great deal of flue dust, probably not any more than the average blast furnace using fine ores, but the amount is out of all proportion to any physical changes in our ores and has never been as low as in some furnaces that are being driven at about the same rate of pig-iron production.

Factors Affecting Flue-dust Production

Every raw material charged into the furnace and every piece of equipment employed in its operation affects the amount of dust carried over by the gas in proportion to its influence on the smooth, regular descent of the charge column and on the chemical reactions that must take place in the blast furnace. When Mesabi ores were first introduced, the frequency of blast-furnace slipping and rolling caused very high losses in furnace yields; but a gradual development of furnace lines and equipment and a better understanding of how furnaces using these ores should be charged and blown, have greatly reduced flue-dust production. In 1902, the blast furnaces of the United States Steel Corpn. used 43.8 per cent. Mesabi in their ore mixtures and the loss in furnace yield averaged 3.6 per cent. During the last 10 years, over 80 per cent. Mesabi has been used each year yet the average loss for that period has been a full per cent. less. In comparing individual furnaces in the same group or comparing furnace groups, however, it cannot be said that any true relationship exists between the furnaces using 60 per cent. Mesabi and those using 100 per cent., when considering the flue dust produced or the loss in furnace yields.

The physical nature of the ores is the primary basis of all ferrous losses in furnace gas but it is rather difficult to compare the aptitudes of various ores to produce flue dust except by actual furnace demonstration. Sieve tests furnish a simple means for rough comparisons but do not distinguish granular, flocculent, or aqueous conditions. The effect of heat absorption on an ore, when driving off the chemically combined water, is far different from that when simply drying up or driving off the absorbed water. The latter is quiescent, whereas the former may be said to be eruptive or analogous to a multitude of infinitesimal explosions, which fairly blow the ore to pieces. Ores that rank well on sieve tests may dust badly on account of their combined water. These actions may be better appreciated by considering the enormous volume of gas produced by the furnace and the quantities of ores reduced during a relatively short period of time. Only the filtering action of superimposed ore charges prevent far greater losses.

The importance of properly grading and thoroughly mixing each grade of ore is readily appreciated when we consider how absolutely essential it is to keep the physical and chemical balance of the slag at all times as nearly constant as possible. Occasionally we are obliged to use raw materials without the guidance of an accurate chemical analysis or without previous knowledge of the physical structure or characteristics. The results on the product and the practice of the blast furnace are invariably detrimental. It usually takes several days of experimenting of an empirical nature to bring the furnace back to normal action, which is only attained by correcting the slag balance. The causes and effects of disturbing this balance with the attendant increase in flue-dust production are too well known for detailed discussion.

I believe that much of the opposition to the use of fine ores in blast furnaces is superficial and prejudicial. Burdens composed entirely of fine ores are being very successfully handled by furnaces built on lines as developed today. High flue-dust production, where prevalent with high percentages of fine ores in the burden, is frequently due to an improper mixing or sizing of the ore. Where no thorough effort is made to counteract the natural segregation of lumps and fines at each rehandling from the mines to the furnace, there are bound to exist in the blast furnaces strata of ore of a finer consistency than contiguous layers. The obvious requirement of these finer and denser layers is an augmented gas pressure, sufficient to force through the denser layer. This action is rather more violent than would be the normal flow of gas and is attended by a greater disturbance of the stock, resulting in a larger production of dust than would follow the passage of the gas through the more open layers of ore. As a means of limiting the segregation of the fines into layers in the furnace, the method of charging is of incalculable value as a corrective feature but is not sufficiently thorough to counteract indifferent handling at the mines and docks. The intimate mixture of each ore into a uniform material physically also brings about a much desired chemical equality.

We acknowledge the existence, from a practical operating standpoint, of an irreducible minimum of flue-dust production for each grade of raw material with a given rate of furnace travel but, especially in the case of granular flue dust, we believe that much of the material now carried over by the gas might be retained by a furnace with ample gas areas in the furnace top and downcomers, as shown in Figs. 1 and 2.

From any view point, coke is the very life blood on which the whole smelting process depends. The physical structure of the coke has a very much greater influence on every phase of blast-furnace practice than has the structure of any of the other materials. As indicating the effect of soft coke on flue-dust production, the following comparative statement is given, covering two operating periods on the same furnace

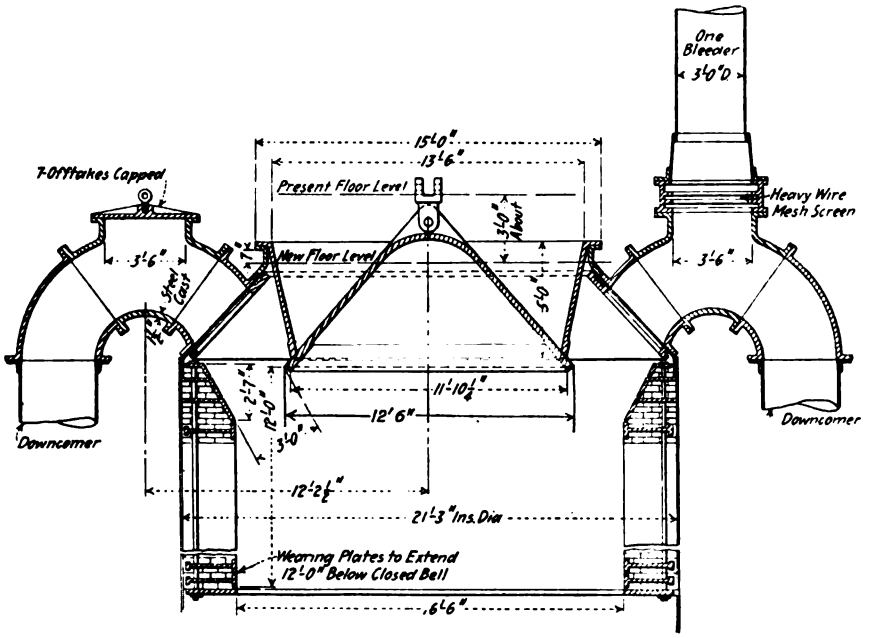


FIG. 1.—PROPOSED FURNACE TOP.

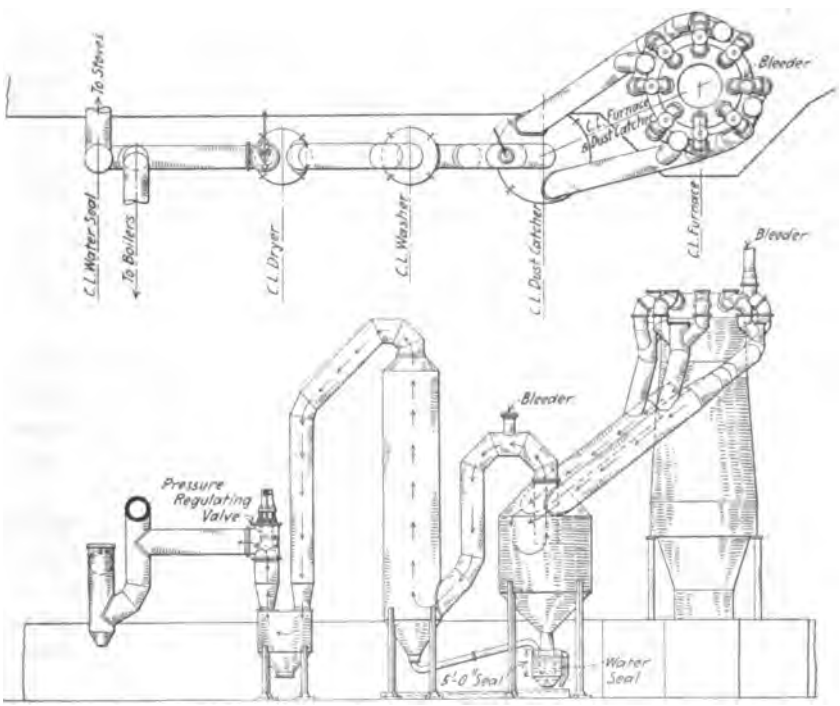


FIG. 2.

under apparently identical conditions aside from the coking time on the byproduct ovens. While using the soft coke, so much of it was dissolved in the furnace stack that it was found advisable to decrease the volume and increase the temperature of the blast and to charge additional coke while it was also necessary to use several times the normal number of scouring charges of bessemer slag to keep the furnace working smoothly.

TABLE 2.—*Influence of Coke Hardness on Flue-dust Production*

Physical quality of coke	Soft and open	Appreciably stronger
Average coking time	18 hr. 51 min.	20 hr. 59 min.
Pounds flue dust produced per ton pig iron	301.9	152.5
Average daily tonnage of pig iron produced	537.6	532.5
Pounds material consumed per ton pig iron produced:		
Coke	2,052.0	2,039.0
Ore, scale, and sinter	4,585.0	4,533.0
Bessemer slag	113.0	39.0
Limestone	1,037.0	1,018.0
Cubic feet of air blown, at 60° F., per minute	43,949.0	44,214.0
Cubic feet of air blown, at 60° F., per pound of coke	57.0	58.2
Blast temperature, degrees F	1,245.0	1,120.0
Blast pressure, pounds per square inch	18.5	18.8
Gas temperature, degrees F	309.0	335.0
Gas pressure, inches of water	30.6	34.0
Average composition of pig iron:		
Silicon, per cent	0.98	0.83
Sulfur, per cent	0.032	0.031
Phosphorus, per cent	0.206	0.179
Manganese, per cent	2.09	2.32
Production over 1.25 per cent., silicon	0.00	0.00
Production over 0.05 per cent., sulfur	0.00	0.00
Composition of slag:		
Silica, per cent	33.43	33.50
Alumina, per cent	15.47	16.11
Sulfur, per cent	1.06	1.02

The results shown for both periods are considerably below the average work of the blast furnace under consideration. About a month after the close of the second period, the coke was still further improved by a change in the coal mixture and the furnace also gained the advantage of a somewhat higher grade ore mixture. It is worth noting the improved results shown in the following statement, except the rate of flue-dust production which increased as the furnace traveled faster in spite of the furnace working very smoothly. Not a pound of scrap of any description was consumed by the furnace during any of these three periods. In any consideration of this nature, it is highly important to exclude from comparison with normal blast-furnace practice the performance of those

furnaces that combine the smelting of iron ore and the cupola function of melting scrap.

Pounds flue dust produced per ton pig iron	196.9
Average daily tonnage of pig iron produced	601.9
Pounds material consumed per ton pig iron produced:	
Coke	1,876.0
Ore, scale, and sinter	4,291.0
Bessemer slag	21.0
Limestone	819.0
Cubic feet of air blown per minute at 60° F	45,208.0
Cubic feet of air blown per pound of coke at 60° F	56.5
Blast temperature, degrees F	1,186.0
Blast pressure, pounds per square inch	19.7
Gas temperature, degrees F	301.0
Gas pressure, inches of water	32.7
Average composition of pig iron:	
Silicon, per cent	1.05
Sulfur, per cent	0.032
Phosphorus, per cent	0.145
Manganese, per cent	1.64
Production over 1.25 per cent. silicon	7.10
Production over 0.05 per cent. sulfur	none
Composition of slag:	
Silica, per cent	32.10
Alumina, per cent	18.75
Sulfur, per cent	1.18

Variable limestone causes irregular operations on a few furnaces but so much high-grade fluxing stone is available at a moderate price that this trouble is usually rectified.

The question of the most suitable lines for our present blast-furnace practice has been discussed so often that I will simply give the general dimensions and results obtained on two furnaces built on about what is now generally conceded to be acceptable lines. The only contrast in operating results is in the remarkably small amount of flue dust produced by the Mark Mfg. Co. furnace. The superintendent, Arthur Baer, gives nearly all the credit to the uniform volume of air supplied by a turbo-blower. The reciprocating engines, for the Inland Steel Co. furnace shown, usually run about 116 r.p.m. The pulsations of the engine strokes can be entirely neglected after the long tortuous course of the blast through the long cold blast mains, large hot blast stoves, hot blast main and bustle pipe. Most blast-furnace men agree with Mr. Baer that his turbo-blower gives some advantage in compensating for atmospheric changes but the dominant effectives in his low dust production are raw materials, furnace lines, and operating methods. This contention is strengthened by the fact that numerous other turbo-blown furnaces show considerably higher losses.

TABLE 3.—*Comparative Blast-furnace Practice*
Period Ending Apr. 1, 1919

	Mark Mfg. Co. No. 1, 3 Months	Inland Steel Co No. 3, 12 Months
Total pig iron produced, tons	52,101	205,353
Average daily production of pig iron, tons	578.9	569.6
Average daily production of pig iron per 100 cu. ft. essential furnace volume	2.59	2.86
Pounds coke consumed per ton iron produced	1,976	1,926
Pounds stone consumed per ton iron produced	901	918
Pounds bessemer slag consumed per ton iron produced	85	22
Pounds ore consumed per ton iron produced	4,323	4,656
Pounds scale consumed per ton iron produced	95	125
Pounds scrap consumed per ton iron produced	42	8
Pounds scrap produced per ton iron	41	134
Pounds flue dust produced per ton iron	73	290
Pounds sintered dust consumed per ton iron	none	72
Average cubic feet air blown per minute at 60° F.	40,688	44,190
Average cubic feet air blown per pound coke at 60° F.	49.9	56.0
Air blown per minute adjusted to 56 cu. ft. per lb. coke	45,660	44,190
Average blast temperature, degrees F.	954	1,002
Average blast pressure, pounds per square inch	16.4	19.7
Number of tuyeres actually blown through	9	12
Size of tuyeres actually blown through	5 in. and 6 in. × 12 in.	5¼ in. × 12 in.
Average gas temperature, degrees F.	334	297
Average gas pressure in inches of water	42	35
Average per cent. of water added to ore charged	none	0.9
Average composition of iron produced:		
Silicon, per cent.	1.04	1.04
Sulfur, per cent.	0.03	0.035
Phosphorus, per cent.	0.19	0.297
Manganese, per cent.	1.09	2.03
Average composition of slag produced:		
Silica, per cent.	34.55	33.23
Alumina, per cent.	14.75	15.92
CaO, per cent.	46.16	44.80
MgO, per cent.	1.98	1.95
Sulfur, per cent.	1.54	1.42
FeO, per cent.	0.46	0.71
MnO, per cent.	0.91	1.97
Per cent. of pig iron over 0.050 per cent. sulfur	2.34	Not recorded
Per cent. of pig iron over 1.25 per cent. silicon	12.39	Not recorded
Per cent. iron between 0.75 and 1.25 silicon and not over 0.04 sulfur	Not recorded	73.39
Method of charging:		
Dump large bell	Coke..... 9,200 Ore.....22,500 Stone..... 4,500	Ore.....14,000 Coke..... 3,700 Stone..... 5,000
Dump large bell		Ore.....14,000 Coke..... 7,400
Essential working volume:		
Height from tuyeres to 6 ft. below bell	71 ft. 2 in.	69 ft. 0 in.
Height from tuyeres to top bosh plates	13 ft. 4 in.	12 ft. 8 in.
Height from top bosh plates to stack batter	5 ft. 9 in.	9 ft. 5 in.
Height of stack batter	44 ft. 0 in.	38 ft. 7 in.
Height from stack batter to 6 ft. below bell	8 ft. 1 in.	8 ft. 4 in.
Diameter nose to nose of tuyere coolers	18 ft. 6 in.	17 ft. 3 in.
Diameter nose to nose of top bosh plates	23 ft. 3 in.	21 ft. 9 in.
Diameter of lining at bottom of stack batter	22 ft. 6 in.	21 ft. 4 in.
Diameter of lining at top of stack batter	17 ft. 0 in.	16 ft. 6 in.
Diameter of lining 6 ft. below closed bell	17 ft. 0 in.	16 ft. 6 in.
Volume calculated from above dimensions	22,371	19,891

TABLE 3.—*Comparative Blast-furnace Practice. (Continued.)*
Period Ending Apr. 1, 1919

	Mark Mfg. Co. No. 1, 3 Months	Inland Steel Co. No. 3, 12 Months
Bosh angle tuyere coolers to top bosh plates	79° 54′	79° 56′
Bosh angle of brickwork	79° 55′	80° 43′
Stack batter in inches per foot	0.75	0.75
Angle of large bell	50°	50°
Diameter of large bell	13 ft. 0 in.	12 ft. 6 in.
Travel of large bell	2 ft. 0 in.	2 ft. 2 in.
Stock line protection plates below bell	12 ft. 6 in.	9 ft. 4 in.*
Stock level below closed bell	4 ft. 0 in.	3 ft. 4 in.
Stock level below bottom of gas off-takes	4 ft. 8 in.	2 ft. 6 in.
Stock level to stack batter	10 ft. 0 in.	11 ft. 0 in.
Closed bell to downcomer openings in uptake	24 ft. 0 in.	24 ft. 0 in.
Total area of gas off-takes in square feet	38.5	38.5
Total area of downcomers in square feet	39.2	35.4
Total area of downcomer openings to dust catcher, in square feet	39.2	30.7
Total area of dust catchers in square feet	254.5	452.4
Total area of gas main exits from dust catchers in square feet	28.3	28.3
Brassert washer	15 ft. × 54 ft. 3½ in.	15 ft. × 54 ft. 3½ in.
Brassert dryer	12 ft. × 16 ft.	12 ft. × 24 ft. 5½ in.
Area of stove gas main in square feet	12.7	28.3
Area of boiler gas main in square feet	38.5	blanked
Area of by-pass to stoves on No. 1 and No. 2 furnaces		9.6
Number of casts per 24 hr.	5	6
Time lost per 24 hr. stopping iron hole	25 min.	11 min.

* Stock line protection plates will be extended to 12 ft. below bell.

The important consideration is not the type of blower but rather the variation in air delivery from one minute to another that causes irregular movement of the stock, with consequent high flue-dust production. This variation of reciprocating engines is especially noticeable at some of the plants where the blast-furnace and rolling-mill steam lines are connected. The steam pressure will vary 25 or 30 lb within a few minutes and no governor on reciprocating engines will govern within two to three revolutions of a given point under varying steam pressure. We will grant that it is difficult to build a governor to answer the requirements of blowing engines but, at the same time, there has been absolutely no improvement in this line for the past 20 years. The governing of turbines has been highly developed to keep step with the exact requirements of electrical generation development. It was a simple step to adapt this governor to a turbo-blower and that, with atmospheric regulation, has given a very valuable blast-furnace air compressor. We are unable to compare the ores used at these two plants, either by analyses or sieve tests, but it is interesting to note that no water is ever added to any of the materials charged into the Mark furnace and none of the flue dust is recharged.

Next in importance, after considering the raw materials and furnace equipment, would naturally be the velocity of the gas as it leaves the furnace; but this question has become rather involved because so few operators attempt to determine the velocity of gas in the downcomers and simply judge the dust-carrying capacity of the gas by the volume of air blown, the blast pressure, or the gas pressure at the furnace top. The causes and effects of high blast and gas pressures are very often misconstrued. A most recent blast-furnace treatise now widely circulated states:

"It is very evident that to secure free and regular settling of the charge, one of the prime conditions is to have the blast pressure low in relation to the weight of the charge column—high blast pressure is an unmitigated evil and in general the lower the pressure with which a furnace will work, the more satisfactory its work will be."

I would take exception to that statement unless qualified by designating the conditions to which the high pressure is due. Large blast furnaces have been operated on very low blast pressures, where the advantages of carrying the slag decidedly acid were permitted to outweigh all other considerations. On the other hand, exceptionally good blast-furnace performance is being made on 20 lb. blast pressure where 4 or 5 lb. of that pressure are due to back pressure from gas washers and gas mains and to a fairly viscous slag and not due to scaffolding of the furnace or improper penetration.

The effect of the density of the gas on ore reduction in a blast furnace holds a large interest. The best operating results have been attained on furnaces with high gas pressures but there is a question whether the intensity of the gases is the direct cause of the difference noted in furnace performance or whether the increased back pressure of perhaps 1 lb. per sq. in. above normal sufficiently increases the blast pressure to materially accelerate combustion of the coke. In this connection, it must be borne in mind that the capacity of gas for carrying flue dust varies as the square of its velocity so that a nominal reduction in the volume of blast blown into a furnace should, and usually does, cause a decidedly decreased flue-dust production; that top pressures normally are a function of the volume and density of the gas leaving the furnace, the frictional resistance of the downcomers and gas mains and the area of the gas-burner openings; that the advantages gained by increasing the furnace area above the point where the charges of raw material strike the furnace wall, thereby decreasing the velocity of the gas and permitting the location of gas off-takes well above the stock level, must be recognized.

Suggested Downcomer Arrangement

Having in mind the foregoing conclusions, we have designed an unusual arrangement of downcomers for reducing the exit-velocity of the gas leaving the furnace, for equalizing the flow of gas over the entire

furnace area, and for controlling the gas pressure inside the furnace. The system is designed so that the gas will travel practically the same distance from each furnace opening to the dust catcher and the swirling effect inside the dust catcher is on a balance as well.

The writer feels that there is no justification for the high gas risers on modern furnaces and suggests a trial of the construction show in Fig. 2. Under this plan, it is proposed to control the gas pressure with a throttling valve on the gas outlet from the last unit of whatever gas-cleaning system is used. At first the regulating valves were placed as close to the mouth of the downcomers as practicable and the off-takes were carefully proportioned so that heavy material would be deflected against the concave

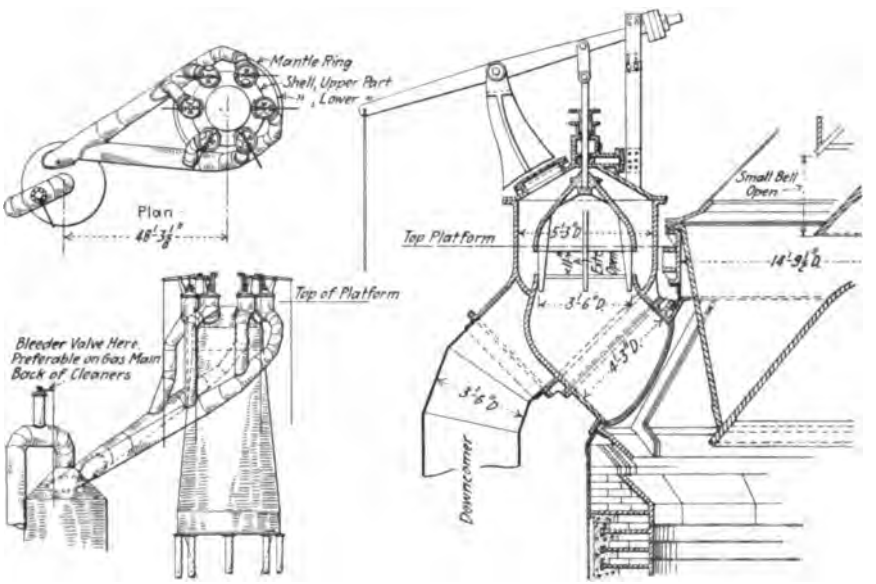


FIG. 3.—PROPOSED GAS-REGULATING VALVE FOR DOWNCOMERS.

surface of the throttling valves and absolutely stopped, causing at least some of it to fall back into the furnace, even against the flow of the gas, see Fig. 3. However, objections to that location developed. It is primarily desired to promote the intensity of the gas without increasing its velocity until after it has deposited its dust in the primary dust catcher and gas washers. Also, it is the intention to have these valves set for the pressure it is desired to maintain in the furnace and yet have them afford relief from the rush of gas following furnace slips or rolls. Throttling valves in the gas off-takes might work so slowly as to endanger the furnace top whereas a valve remote from the furnace would utilize the receiver effect of downcomers, dust catcher, and gas washers, thereby dissipating the force of violent slips.

Utilization of Flue Dust

Volumes have been written describing the various methods of removing flue dust from furnace gas. The writer believes steel-wool gas cleaners will be developed to practical usefulness but, in the absence of this development, favors the tower type of wet washers such as the Zschocke, Diehl, or Brassert. It is true these washers waste the sensible heat of the gas but they have proved to be wonderfully efficient and reliable gas cleaners. As a further development, the writer believes we shall discover a combination of flotation and hydraulic concentration of gas-washer sludge that will wash the coke dust out of the flue dust and furnish a material no more difficult to reduce in furnaces than is the finest ore. This may possibly be accomplished by some elaboration of the Dorr thickener. The dust thus concentrated could be pressed into briquettes for open-hearth furnaces or used to advantage in the manner suggested by Mr. Brassert for utilizing washer sludge by piping it to the skip pits where a measured amount is added to each skip of ore.

The loading, transporting, and unloading of hot flue dust has caused so many serious accidents, is such an expense, and makes it so nearly impossible to keep a furnace plant clean that even the material deposited in primary dust-catchers should be sluiced continuously from the catcher direct to the settling basin, as shown in Fig. 2.

About 12 years ago, at the Bellaire furnaces of the Carnegie Steel Co., we converted the dust catchers into rough contact washers by filling the cone sections with water constantly discharging through a water seal constructed of standard pipe fittings. The object was to increase the gas-cleaning efficiency of the dust catchers but, at the same time, a more desirable method of handling the flue dust was gained. By allowing the heavier dust to settle, enough of the coke dust was floated off as lighter material to permit the successful recharging of all flue dust recovered. This condition prevailed even when the 12 ft. and 12 ft. 6 in. hearth furnaces were driven to an average production of over 400 tons of iron per day, in spite of increased production of flue dust and a coincident consumption to as high as 400 lb. of flue dust per ton of iron produced. It would seem that the plan of washing out the coke dust has generally prevailed wherever flue dust has been successfully recharged. Such an assertion would also explain the superiority of weathered stock-pile dust. J. W. Dougherty's proposed method of feeding raw dust through the furnace shell, by means of a worm gear, was given some publicity a few years ago, but it is so nearly a mechanical impossibility to introduce any material below the stock level of a furnace and yet distribute it uniformly over the full furnace area that his suggestion was never considered seriously.

It is well known that flue dust contains carbon sufficient to sister it readily (in either the Dwight-Lloyd or Greenawalt machines) into an

excellent material for adding to the ore burdens. Briquetting by using some binding material or sintering action, direct roasting, or sintering and nodulizing in rotary kilns are all in practical operation. While the product of these heat-agglomerating processes has a tendency to make the furnace charges more open, it also has a disadvantage in the important consideration of fuel economy. These products invariably are formed as silicates of iron and as such form the most irreducible material that is charged into the blast furnace. In general, we may say that no one but the actual operators can begin to appreciate the countless difficulties encountered in attempting to handle flue dust efficiently and economically for any of the foregoing processes. In the first place, if the dust is handled on a purely manual basis, the labor cost becomes prohibitive. Secondly, if elaborate and expensive machinery is installed to get away from the high labor cost, the wear and tear on the machinery prevents the success of the plan. But we may safely say that the cost of any of these processes is far in excess of that for simply floating off the coke dust. The value of the hydraulic concentration method depends on the writer's hypothesis that the coke dust is really what causes our blast-furnace operating difficulties when raw flue dust is recharged. There is much evidence that neither the extreme fineness nor the fact that it is highly magnetic would preclude returning the concentrated flue dust direct to the blast furnaces.

Debarring furnaces that consume more scrap than they produce, it is a very general impression that maximum blast-furnace production can only be attained at a considerable sacrifice of fuel economy and excessive loss in the yield of the ores. The writer operated two furnaces that, for a period of more than a year, consumed (untreated) all the flue dust recovered from their current operations. During that period, 80 per cent. Mesabi ore was used. Both the pig-iron production and the coké practice were highly creditable. In operating other furnace plants, the writer has been unable to satisfactorily utilize the flue dust except through sintering. Blast-furnace operators hold such a diversity of opinions on all furnace problems that it seems rash to claim they are ever in accord, but I have never heard the claim advanced that all raw flue dust is equally objectionable material. The writer cannot conceive of any reason why wet flue dust fairly free from coke dust should disturb any of the functions of a blast furnace. He also believes the suggested reduction in velocity and the pressure control of the gas leaving the furnace would afford very decided operating advantages.

DISCUSSION

C. A. MEISSNER, New York, N. Y. (written discussion).—As Mr. Atcherson says, flue dust is a very vexing problem. If not eliminated from our gas it makes dirty stoves, dirty boilers, and inefficient combus-

tion, with frequent interruptions through cleaning of stoves, etc. If eliminated, its handling is apt to be a nuisance. If taken out with the wet process we have a sludge that, while it can be thickened by settling or in Dorr thickeners, or similar apparatus, comes to us in a mass with at least 50 per cent. of water which must be removed. If the dust is taken out dry, and there are as yet only three dry processes that can be considered, hot dry flue dust is not always easy or safe to handle. The three dry-cleaning systems that offer some chance of success are the old German Halberger-Beth bag cleaning system, the Kling-Weidlein shaking mattress, and the Cottrell electric system. I would also call attention to the paper by W. A. Forbes on the cleaning of blast-furnace gas.[1]

In whatever form we receive the flue dust from the gas, it must be cared for in some manner, as we cannot afford to lose it, nor are we permitted to let it pollute our waterways.

The easiest form for reusing the flue dust is to put it back as raw dust; as Mr. Atcherson shows, this has been done on a large scale, with a certain amount of success. My experience has been that blast furnaces using raw dust after a while slow down their production. The coke consumption may be held about where it had been and there may be a lessening of costs, which is natural if the value of the flue dust is not charged a second time, except for handling costs, on the ground that it has already been paid for as ore and coke, but the furnace will not, as a rule, give the same production of pig iron.

Furthermore, the condition of the furnace and, especially, the lines of the furnace are very potent factors in the ability to re-use raw dust without disturbing influences on the furnace. When a furnace is running well and freely and perhaps carries a certain amount of scrap, two furnaces in a plant have taken more flue dust than they made, while two other furnaces of the plant, which were not in as good a condition of operation or lines, would immediately show trouble if a large percentage of raw dust was used. Furnaces with more modern lines—large hearths, steep angles, and low boshes—can carry practically all the flue dust made, because, first, the tendency is to make less dust by more smooth operation due to the better lines and, second, they will absorb more deleterious materials, such as raw dust, more freely. There is one thing certain: when a furnace refuses to operate properly when all its dust is being returned to it, serious trouble will occur if an attempt is made to force this furnace to take all its dust.

Mr. Atcherson has gone very fully into causes of dust, and the fact that the dust from Mesabi ore furnaces shows 45 to 50 per cent. of iron plainly indicates that it comes from the ore as well as from the coke. Whether the scheme of using dust catchers outlined by Mr. Atcherson

[1] *Trans.* (1913) **47** 357.

will materially lessen the formation of the flue dust is a matter that must be tried out.

A good sintered dust is more satisfactory than raw dust; it always seems absurd to me to take great precaution to screen the dust out of the coke and then put coke dust from the flue dust into the furnace; even though it may be said that in the one case the dust from coke may be supplied irregularly, while the dust from the flues is put in in regular proportions. Anything in the shape of fine coke dust has a tendency to be amalgamated, or partly fused, with the slag and makes a very infusible material of carbon and slag, not permitting the air to obtain access to the carbon in such a way as to produce combustion.

H. A. BRASSERT, Chicago, Ill. (written discussion).—The problem of flue-dust prevention must find its solution largely inside of the furnace; that is, in the stock column rather than above it. Proper proportioning between brick lining and bell to reduce the gas velocities through the stock as it falls off the bell, as described by Mr. Atcherson, may be quite effective in the case of furnaces making fairly large amounts of flue dust; yet, we can influence the flue-dust production but little by increasing the areas above the stock line and in the downcomers, or by using higher uptakes. If the principles involved there are carried to extremes, they will be very effective but our efforts in this direction will soon be halted by the limits of practical furnace design. In other words, the source of flue dust is in the stock column and its prevention must occur there. Constructive features above the stock line, generally speaking, only function to recover flue dust already made, returning it to the stock column where part of it is bound to repeat the cycle.

The raw materials are the first cause of flue dust, but the furnace lines or the operation, as affected by the method of charging, the heat and blowing practice, will cause large or small production of flue dust. If we can so adjust the furnace construction and operation that the descending column will settle continuously and smoothly, without jerks and with the ascending gas distributed minutely and uniformly through the stock, we will produce the smallest amount of flue dust. To explain it in the language of the practical furnace man, we must prevent the furnace from hanging and slipping on the one hand and from channeling on the other. These two conditions are not easy to combat at once, as the methods that prevent the one may cause the other, if carried too far. For instance, by too much batter in the inwall we decrease the wall resistance but invite channeling of the gases up the walls. Too acid slags, or the improper amount of wind blown, or coke and stone of uneven and too large size to match the fine ores may reduce the resistance in the stack, causing the charges to move smoother and faster but there will be greater flue dust production.

The raw materials used should not contain or tend to evolve too high a percentage of fines and at the same time they should be devoid of large pieces. What is wanted is uniformly small ore, coke, and stone which, while increasing the resistance to the rising gas column, will make a finer filter bed than a burden composed of coarser raw materials. This finer filter bed will not only intercept more dust, but less dust will be made by the larger number of small streams of gas than the fewer number of larger ones.

The resistance in the furnace that the descending column has to overcome is fairly well measured by the blast pressure. As the late J. E. Johnson, Jr., pointed out, considerable of the weight of the charges is carried on the blast. It naturally follows that the charges will move more readily with low pressures than with high. The effective pressure is the differential pressure between top and tuyeres. I agree with Mr. Atcherson that high top pressures are not detrimental to the working of the furnace and have the effect of accelerating the reduction and combustion process, although only to a slight extent, as at best such influence can only produce a result directly proportioned to the absolute pressures. Even if the top pressure were raised to twice that given by Mr. Atcherson, or from 35 to 70 in. water, it could not affect the reactions in the furnace hearth more than approximately 4 per cent.

The blast pressure, while largely depending on raw materials, basicity of slag, and other operating conditions, can be lowered by changing the furnace lines. For instance, flatter boshes will decrease the blast pressure by carrying the weight of a larger portion of the stock column. But this is apparent only as long as the furnace is working normally. A flat bosh will eventually build up, throttle the descending column, and cause high pressure, hanging, and slipping. Therefore, flat boshes are not to be recommended as a means of maintaining low blast pressures, so we have looked in another direction to decrease the resistance in the stack and that is by lower gas velocities throughout.

The lower gas velocities were obtained by means of wider stacks, larger inwall batters, and larger, but short and steep, boshes. By lowering the bosh and keeping the bosh angles steep, we have minimized the throttling effect on the stock column and placed it where, with careful heat practice, it can be kept harmless within the melting zone. With the increased batter in the inwall, the friction of the charges on the walls has been lessened, keeping them in steady motion and preventing carbon deposition, which is one of the most serious causes of hanging. It would seem that with our present low boshes (10 ft. above tuyere level and a batter of ¾ to 1 in. to the foot) the wall resistance has been almost eliminated as a serious retarding factor.

The gas velocity in the stack is thus lowered by the increase of the average cross areas of the stack below the stock line and because of the

opening of the interstices in the stock column. Unquestionably the settling of the charges into the larger and larger areas of a stack with a big batter must have the effect of loosening up the column, causing a total larger area of interstices, thereby lowering the velocity of the gases.

What is desired, of course, is not only a low average velocity with a given rate of driving, but a velocity uniformly low at every point in the stock column. To secure this, the distribution of the materials must be good from the start; the big batter then eliminates interference with their settling evenly on the way down, permitting no sticking to the walls here and running ahead there, and preventing classification or separation of coarse and fines. The newer method of mixed charging lends itself better to our purpose than the older method, where greater masses of ore were deposited together and had more chance to become packed, having greater adhesion between particles than if they had been mixed with the lumps of coke and stone.

Since with our present bell arrangement we cannot materially increase the stock-line diameter and still obtain desirable distribution, our largest furnaces adhere fairly closely to a 17-ft. stock line, which gives sufficiently low velocities. A 1-in. batter in the inwall leads to a very large bosh and to a correspondingly large hearth, as we must maintain the low and steep bosh. In this way the modern Mesabi furnace, big at the bottom and in the bosh and drawn in to a comparatively narrow stock line, has been developed.

By comparing outputs of various furnaces with their cubical capacities, and creating a standard of performance on this basis, there has been an incentive to strive for large tonnages per hundred cubic feet capacity by building narrow stacks of comparatively small cubical content. This has had the tendency to retard the development of the best furnace design for Mesabi ores. To make real progress in the use of these fine ores, we must so design the furnaces that they will work without effort. In other words, they must be large so that they will make big productions easily with low gas velocities, low pressures, and low flue-dust production.

Mr. Mathesius, at South Chicago, has developed this idea most fully. Other furnace men have increased their boshes to very large diameters, but at the expense of flattening them or increasing their height. As a result their boshes became too prominent and they lost the advantage gained by the larger diameter and greater batter of the stack. Mr. Mathesius was the first man to couple the larger bosh with the proper size of hearth. In the fall of 1917, he remodeled the No. 6 furnace at South Chicago with a 23 ft. 6 in. bosh and a 20 ft. 9 in. hearth, with a 1 in. batter of the inwall. This furnace has had a remarkable record averaging over 600 tons per day for more than a year without the use of any scrap, and is working with the most uniform blast pressure I have seen, and a lower pressure than furnaces of the same height working in the same group.

But the most interesting feature of the performance of this furnace is that it has been burdened right along with 10 per cent. Mesabi ores, besides using 4 to 5 per cent. of raw dust, yet the flue-dust production has been no higher than in the other furnaces.

The question is, how far can this development be carried? Is it possible to increase the batter still further relying on the materials to settle uniformly toward the walls and opening up the interstices in the stock column uniformly, without creating larger voids that might induce channeling of the gases?

The attempt to loosen the stock column by excessive batter must be approached with great caution and then only in connection with fine ores of characteristics similar to the Mesabi's. Fine ores that do not pack, nor swell through carbon deposition, and which require longer reducing periods, such as magnetic ores, cannot be successfully handled in furnaces designed for fine hematites. In fact, the best practice on eastern magnetites has developed the opposite tendency in regard to shape of the furnace stack from the bosh upwards; small batters and greater height relative to diameter has proved the better design to prevent the fines from running ahead and to give them proper time for reduction.

Regardless of ores, the success of any furnace development depends, as Mr. Atcherson has stated, in the first instance on the quality of the coke. Friable cokes that break into small pieces, excessive breeze, and dust will cause uneven distribution of coarse and fines, channeling and packing, and high pressures and high velocities in the channels where the gases break through; in other words, the most favorable conditions for creating flue dust. Good clean coke of uniform size is always the first essential for low flue-dust production.

In studying the subject of flue-dust production care must be taken not to judge a furnace operation by the commonly used practice-sheet term "flue dust produced," which really should be "flue dust recovered." A furnace having good flue-dust practice may have a very efficient dust-collecting plant and on that account will make a poor showing on a comparative sheet against a furnace with no better practice, but a very inefficient dust catcher system. With the modern improvements in wet gas cleaning, with the new filtration methods, and particularly with electrical precipitation, we will recover a higher and higher percentage of the dust produced in the furnace. I would suggest that the furnace operation in reference to flue-dust production be judged by the furnace loss; that is, the difference between actual and theoretical yield, and that the term "flue dust produced" be changed to "flue dust recovered." Also the theoretical yield should be calculated upon the metallic contents of all iron-bearing materials, including raw as well as the treated flue dust, for the present method puts the penalty of higher yield loss on the furnace man who sinters his flue dust.

The great size of the unit, its enormous cost, the large requirements of raw materials, and the long life of a lining, which gives the blast-furnace operator or designer no chance to correct his error for several years, place a responsibility on his shoulders that is equalled in no other industry. Therefore, he needs all the encouragement of a practice and cost sheet system which will reward his efforts for progress and ultimate efficiency.

Measurement of Blást-furnace Gas

By D. L. Ward,* Chicago, Ill., and R. S. Reed,† Ashland, Ky.

(New York Meeting, February, 1921)

This paper is the result of a study, in 1919, to determine how much surplus power could be produced through the proper utilization of the entire gas flow from the two furnace stacks at the Federal Furnace Plant, South Chicago, Ill. Obviously, the problem was to measure the flow of gas through the main beyond the point where the amount necessary for stove operation was removed. In all probability, blast-furnace gas is the most difficult gas to measure, because of the high moisture and dust content, and the widely fluctuating flow from the furnaces. This wide fluctuation of flow forbids the acceptance of any one group of flow readings as indicative of normal operating conditions.

A study of the conditions showed that a recording device on gas flow was necessary. As the gas at the point of measurement had passed through wet washers, and accordingly was saturated with water and contained considerable dust carried past the scrubbers in the form of sludge, no form of Pitot tube could be used, for this sludge would quickly plug the dynamic and static holes, spoiling the gage readings. An even more serious objection to the use of Pitot tubes was the impossibility of accurately measuring the cross-sectional area of the gas main on the plane of Pitot-tube installation. Given an absolutely clean gas and a perfectly circular pipe, it would be safe to assume, through measurements of the pipe diameter, that the gas main was of a certain cross-sectional area. But the continual depositing of sludge and the fact that the main was fabricated from riveted sheets led us to discard the idea of using Pitot tubes for this service.

The Venturi tube was then considered, and had there been a sufficiently long straight run of gas main to accommodate a tube of the required size (72 by 28 in.) such an installation would very likely have been made.

A plate with a sharp-edged orifice was eventually accepted as it possesses all the characteristics of a Venturi tube, requires less space, and

* General Superintendent, Federal Furnace Plant, By-products Coke Corpn.
† With Semet-Solvay Co.

is much easier and cheaper to install. Besides, sludge deposits do not tend to affect the diameter of a sharp-edged orifice as greatly as the throat of a Venturi tube, and it is reasonable to assume that sludge deposits are more easily removed. Accordingly a plate with a 43-in. (109 cm.) orifice was installed in the 72-in. (182.9 cm.) main in connection with an indicating-recording-integrating meter. This instrument has been in use over ten months and has given no trouble to operate or maintain. The sample chart, Fig. 1, shows that a sensitive legible record is obtained from every fluctuation in gas flow.

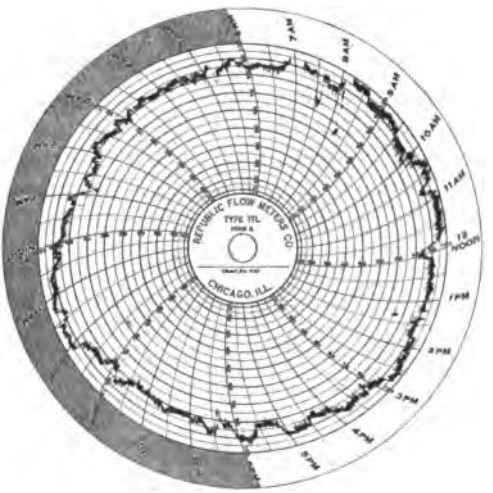


FIG. 1.—SAMPLE CHART SHOWING FLUCTUATIONS OF GAS FLOW.

When originally installed, the instrument was designed to operate on a maximum differential pressure across the orifice of 3 in. (7.6 cm.) of water. At this differential the flow rate would be about 3,000,000 cu. ft. (84,950 cu.m.) per hr. Later, when two furnaces were put in operation, it was found that a greater amount of gas would be produced so the float was arranged to operate under a maximum differential of 4½ in. (11.4 cm.) of water.

THEORETICAL CHARACTERISTICS OF ORIFICE

The flow of gas through a properly designed orifice takes the same form as through a Venturi tube, but, owing to the sudden change in cross-sectional area, the smallest section of gas occurs after having passed through the orifice. As shown in Fig. 2, the gas flow having an initial velocity of v_1 and a corresponding static pressure of p_1 is forced through an orifice and its velocity increased to v_2. This increase in velocity, which is maximum at the point of greatest contraction xd, produces a static pres-

sure p_1 lower than p. In other words, a certain proportion of the initial pressure p is converted into velocity pressure due to the constriction introduced in the gas main.

The formula that has been developed is as simple and reliable as necessary for determining the flow of gas through an orifice. It is as applicable to Venturi or Pitot tubes if the proper value for c is substituted.

$$Q = CA\sqrt{2gH}$$

where Q = flow of gas, in cubic feet per second;
C = coefficient of flow;
A = area of orifice, Venturi throat (or pipe section if Pitot tube), in square feet;

$$H = \frac{T \times 225 \times h}{P \times D}$$

where T = absolute temperature of gas, in degrees C.;
h = differential pressure, in inches of water;
P = absolute pressure of gas, in millimeters of mercury;
D = specific gravity of gas referred to air.

For Venturi tubes C, the most important and variable value, has been generally accepted as 0.95 to 0.99; it usually varies directly as the ratio

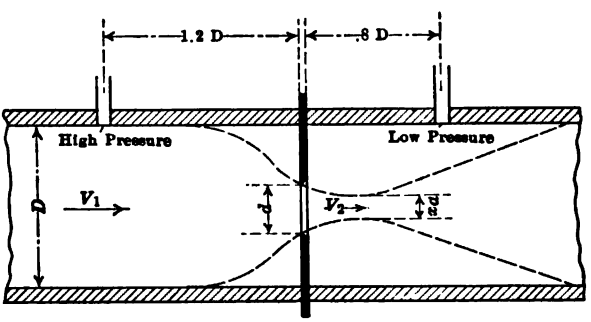


FIG. 2.—CHARACTERISTICS OF GAS FLOW THROUGH ORIFICE PLATE AND LOCATION OF PRESSURE CONNECTIONS FOR RECORDER.

of the throat diameter to the upstream pipe diameter. For Pitot tubes, the value C varies anywhere from 0.5 to unity, due to the many different types of Pitot tubes used and their relative location in the gas flow. In some cases traverses of the gas main are made in order to obtain an average velocity reading; in others, the tube is permanently located in a certain position and the value of C adjusted accordingly.

For an orifice-plate installation, the curves developed by J. M. Spitzglass for determining the value of C, shown in Fig. 3, were used. An inspection of these curves will show that as the diameter of the orifice approaches the diameter of the pipe in which it is installed, the value of C approaches unity. Nearly all authorities agree that it is best to keep

the ratio of the orifice to the pipe diameter below 0.66, and some set the limit at 0.50.

The following calculations show the application of the gas-flow formula to observed conditions at the Federal furnaces with one furnace in operation:

D, or the diameter of the gas main, is 72 in. and d, or the diameter of the orifice, is 43 in., therefore

$$\frac{d^2}{D^2} = \frac{1849}{5184} = 0.35$$

The value of 0.35 as shown on the curve is 0.67, which is the value of C. A = 10.08 sq. ft. and $\sqrt{2g}$ = 8.025.

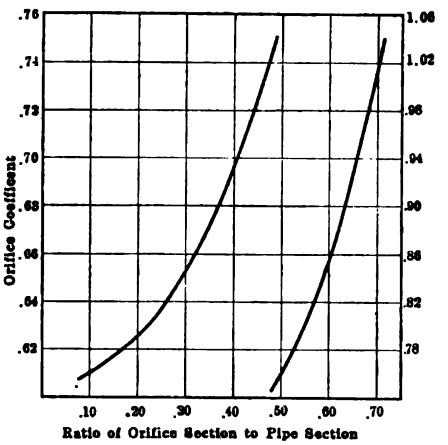


FIG. 3.—CURVES FOR DETERMINING VALUE OF C FOR AN ORIFICE-PLATE INSTALLATION.

As observed temperature of gas is 17° C., absolute temperature, or T, is 273° + 17° = 290° C.

h, or differential pressure, is 2 in. water. As the static pressure is 30 in. water, or 56.1 mm. mercury, P, or the absolute pressure is 757.9 + 56.1 = 814 mm. mercury.

D, or specific gravity of blast-furnace gas, is practically unity.

Hence $Q = 0.67 \times 10.08 \times 8.025\sqrt{H}$.

$$\text{As } \sqrt{H} = \sqrt{\frac{290. \times 225. \times 2.0}{814. \times 1.0}}$$

$Q = 54.17\ \sqrt{160}$ = 685.25 cu. ft. per sec. = 2,466,900 cu. ft. per hr (69,854.4 cu.m.)

In order to test the accuracy of the gas-meter installation, it was decided to calculate the theoretical yield of gas from the furnace and run a short test by diverting the entire gas flow through the boiler-house

gas main. To do this, it was necessary to shut off the gas flow to stove burners and then measure the increased gas flow through the orifice. The method employed for calculating the gas yield was that outlined by Richards.[1]

Let L = limestone charged per day, in pounds;
C = coke charged per day, in pounds;
F = flue dust collected per day, in pounds;
P = pig iron produced per day, in pounds;
A = carbon, by analysis, per cent;
B = CO_2, by analysis, per cent.

The percentage of carbon in the flue dust, coke, and pig iron is found and the percentage CO_2 in limestone; in the latter case due account is made for the $MgCO_3$ content. The theoretical amount of carbon converted into gas may then be found thus:

Carbon converted to gas, lb. = $(0.27281\,LB + CA) - (FA + PA)$.

It is then necessary to analyze the furnace gas and calculate the amount of carbon in each cubic foot of gas; generally this value will be between 0.012 and 0.0155 lb. (0.0054 and 0.007 kg.) per cu. ft. If this value is divided into the figure obtained from the formula, the theoretical gas yield per day may be calculated. At the Federal plant these analyses and calculations were used with the production figures over 24-hr. periods; the resultant figures were very consistent, and, during tests made with the orifice meter, checked the gas-flow figures very closely. Sometimes the 24-hr. results were not in line with the flow-meter figures; at other times, the two methods checked within several thousand cubic feet of gas per 24 hr. However, when the figures were tabulated, averaged, and compared over one or two weeks' period of time, the results were very satisfactory.

This goes to show the value of blast-furnace gas flow tests and records covering a considerable period of operation, and the comparative inaccuracy of gas flow tests of short duration.

DISCUSSION

R. S. Reed.—The gas will carry water vapor in proportion to its temperature. Beyond 212°, the amount of water vapor carried will be infinite, so that when measuring the hot blast-furnace gas, to reduce that gas to a dry gas basis, the amount of water vapor it is carrying must be determined. The best way of doing that is to pass the gas through a sulfuric-acid train. But in the case mentioned the gas passed through washers and so was practically a saturated gas at that temperature which was approximately 70°, at which temperature we tested and estimated that the gas would carry 1 lb. of water per 1000 cu. ft.

[1] "Metallurgical Calculations," Part II, Chap. III.

J. W. RICHARDS,* South Bethlehem, Pa.—But the pressure of the water vapor in the instrument is taken into consideration.

R. S. REED.—Yes.

J. W. RICHARDS.—It is only for reducing to a dry-gas basis the volumes given by the meter, that allowance is made for the moisture content.

R. S. REED.—Yes.

OWEN R. RICE, Bethlehem, Pa.—You show that the pressure difference is about 2 in. of water. Frequently we have been obliged to operate on very low gas pressures, what is the percentage of drop under a pressure of ¾ or ½ inch?

R. S. REED.—The orifice must be designed to suit the conditions. In other words, if the total static pressure is limited the size of the orifice must be increased so that the pressure drop through there will not be too great. In the case cited, the pressure drop was 8 per cent. of the observed static pressure.

OWEN R. RICE.—Operating under those conditions, would not an orifice of considerable size so far detract from the accuracy of the method that a Pitot tube would answer as well?

R. S. REED.—We found that when the gas is not clean the openings in the Pitot tube plug up immediately and it is impossible to tell how these deposits are affecting the cross section of the opening.

J. W. RICHARDS.—I have not used the Pitot tube on blast-furnace gas, but on other dusty gases two careful experimenters may be as much as 50 per cent. apart in their determinations. This difference is due to the clogging of the tube by the dust and also to the shape of the downstream orifice, which is supposed to register the static pressure. A simple form of meter, such as this, has been needed ever since there has been a blast furnace. The fact that the ratings check with the balance sheet of the furnace and the gas as determined by analysis is extremely satisfactory, because it proves that the instrument is doing its work.

R. S. REED.—The small ordinary Pitot tube is not difficult to handle, but in a main 6 ft. in diameter it is a problem to be sure that the static-pressure openings will give only the static pressure.

J. W. RICHARDS.—Have you considered the possibility of using this meter on the blast side of the blast furnace to measure the amount of air that the furnace is receiving?

* Professor of Metallurgy, Lehigh University.

R. S. REED.—The company that built this meter, I believe, was contemplating the installation of such a device for one company to measure the blast of the blowing-engine manifold.

J. W. RICHARDS.—Probably the amount of gas that the furnace receives is of more importance for the running of the furnace than the amount of gas it produces. We know that the blast-furnace manager's statements as to the amount of air which the furnace is receiving are usually accurate only within from 10 to 50 per cent.

Recently the General Electric Co. devised a blowing engine on which is a regulator and a measurer, which it is claimed will give quite exactly the amount of air going through the furnace. The company has checked up the results with the statements of blast-furnace managers as to the amount of air their furnaces were receiving and has found that the apparatus shows that the furnaces are usually receiving from 10 to 30 per cent. less than the managers supposed. The reason for this discrepancy is that on a reciprocating cylinder engine, the piston displacement is known, but the percentage of air that gets into the furnace is usually unknown. The blast-furnace manager usually says, "It will show 90 per cent. efficiency of delivery," while the efficiency averages probably more nearly 75 or 80 per cent.

The General Electric Co. has used this meter on its centrifugal blower on several furnaces and compared the readings with the amount of blast by the balance-sheet method; there was a difference of about 5 per cent. If a simple device like this, put on the blast side of the blast furnace, will give accurately and continuously the amount of air blown, the blast-furnace manager will find it at least of equal value to that side of the furnace.

W. H. FULWEILER,* Philadelphia, Pa.—Did the high- and low-pressure orifices extend completely around the main or were they taken from one point? Some work that we did showed that unless care was taken in the location of these orifices erratic results were occasionally obtained.

R. S. REED.—The upstream and downstream pressure pipes were located at three points in the main and connected with a pipe. They were not put in the bottom because of the dust accumulation, but on each side at a horizontal plane. They went into a large bustle pipe, and then led off from there.

W. H. FULWEILER.—Some work that we did with Venturi tubes indicated that six openings gave more accurate results than four. The errors introduced depend on the flow of the gas; that is, the previous history of the gas, the number of bends, and their proximity to the meter.

* Chemical Engineer, The United Gas Improvement Co.

By plotting the errors against the velocity, we found that they were rather erratic, that the error at one velocity would not be the same as an error at another velocity. This we thought was caused by the vibrations in the gas stream as the nodes and antinodes do not coincide at different velocities.

J. W. RICHARDS.—The diagram shows that the openings are at right angles to the stream flow; were the openings as shown or was there a device inside any particular opening directing the flow at right angles to or away from the current of gas?

R. S. REED.—The openings were all at right angles to the flow.

J. W. RICHARDS.—If any inaccuracies were found, the location of the terminals of those outlets might be studied to see if an error is produced by having them just plain openings.

R. S. REED.—They should be studied for each particular case. The effect of the bends in the pipe must also be considered.

The Acid Bessemer Process

RICHARD S. MCCAFFERY,* E. M., MADISON, WIS.

(Lake Superior Meeting, August, 1920)

THIS paper considers certain aspects of the acid bessemer process, particularly in its relations to the duplex process—that combination in which the pig iron is first desiliconized and decarburized in acid bessemer converters and then dephosphorized in basic open-hearth furnaces. The acid bessemer process employs an acid-lined converter and produces an acid slag. The blow is usually thought to eliminate the silicon and manganese as oxides and then to burn off the carbon as carbon monoxide On account, however, of the relatively large amount of metallic iron present in the converter, compared with the relatively small amount of the impurities it is desired to oxidize, the first reaction in the converter probably is the formation of iron oxide, which dissolves in the bath and acts as an oxygen carrier for the silicon and carbon. As soon as iron oxide is dissolved throughout the bath, the oxidation of silicon commences; but in the early stages of the blow the mass law would indicate that iron oxide must form first, and this oxide probably increases up to some saturation point. The molten metal in the converter from the early stages of the blow right through to its completion remains basic, while the slag produced is siliceous. This fact is shown by the corrosion of the acid bottom and the tuyeres, which is greatest at the tuyere orifice where oxidation is most active and where there is the most iron oxide.

Why does this acid bottom corrode? Because it is attacked by a base. The thought, therefore, suggests itself, why not make the bottoms of basic or neutral material?[1] As the converter slag is acid, those parts of the converter coming in contact with the slag should be acid; but those parts of the converter that are in contact with the molten metal saturated with metallic oxides should be basic or neutral. Bessemer operators have for some time tacitly admitted this condition, for the blast pressures have steadily increased with the object of keeping the metal in suspension, and so preventing bottom corrosion; if the molten metal were not basic, it would not attack an acid bottom. In addition, the tuyeres are bunched together at the middle of the bottom and a clear space is left around the outside of the bottom; if tuyeres are placed too near the side walls the

* Professor of Metallurgy, University of Wisconsin.

[1] The use of basic and neutral material for making the bottoms in acid-process steel converters is protected by U. S. Patent, No. 1338655, issued Apr. 27, 1920.

wall corrosion increases. If the increase of blast pressure in bessemer converters was for the sole purpose of hastening the blow by getting more oxygen into the converter in the same time, the number of tuyeres might have been increased, thus increasing the volume of air and decreasing the blast pressure. It is not desirable though to follow this procedure, because the additional tuyeres can be provided only by placing them near the side walls, which results in increased lining costs.

In a normal blow, the carbon stage begins after the oxidation of the silicon, the carbon burning largely to carbon monoxide; it thus does not generate sufficient heat to raise the temperature of the bath during the latter part of the blow; the great rise in bath temperature takes place in the early stage when the silicon is burning. Many converters, though, particularly those of larger capacity, do not blow a charge in this way; they show a temperature rise during the latter part of the blow, the carbon being burned to dioxide instead of to monoxide, with the resulting liberation of 97,000 calories instead of 29,000 calories. As a matter of fact, many blows that are not initially of too high silicon contents are finished at excessively high temperatures, in some cases running up to 1800° C. Although the bad effect of this practice is known and attempts are made to lower the final temperature by the addition of scrap to the converter or by the introduction of steam in the air blast, the best method of lowering this temperature, by burning the carbon to monoxide, which also decreases by one-half the power consumption during the carbon stage of the blow, is not used because it is necessary to keep the metal charge away from the converter bottom. By following the present practice, the direct bottom expense may be reduced seemingly by employing a high blast pressure, but the power cost is greatly increased and the temperature of the finished blown metal is very high; or if the finishing temperature is kept down to the proper point, there is the extra expense of scrapping or of steaming. It does not seem right to charge scrap in a process that has as one of its principal objects the production of scrap, or to expend energy for excess air in order to turn carbon to dioxide when the extra amount of air will be furnished by the atmosphere at the converter mouth. By this plan a vicious cycle is in operation: more energy is employed for blowing in more air, which produces more heat, which requires more energy, in the form of steam, to lower the temperature. With the use of basic or neutral bottoms, blast pressure may be reduced and the tuyere area increased because the basic charge will not corrode bottoms of this character. The actual blowing time then can be materially shortened, no scrapping or steaming is necessary, and a colder blown metal is produced.

The author has already pointed out[2] the possibilities of decreasing the

[2] *Iron Age* (1919) **103**, 626.

time of blow and decreasing the power consumption with the use of a greater number of tuyeres and lower blast pressure; and Table 1 summarizes the data obtained in a test of a 23-tuyere bottom compared with a bottom designed by the writer containing 35 tuyeres.

TABLE 1.—*Results Obtained by Increasing Number of Tuyeres and Decreasing Blast Pressure*

	Old-style Bottom	New-style Bottom
Number of tuyere blocks, each containing twelve 5/8-in. tuyeres	23	35
Weight mixer metal, pound	47,000	50,000
Blast pressure at engine, lb. per sq. in	28	22
Total engine revolutions per blow	589	443
Time of blow, minute	14	10½
Comparison of time, per cent	100	69
Comparison of power, per cent	100	60

In the open-hearth stage of the duplex process, the temperature of the open-hearth bath is an important factor if the dephosphorizing operation is to be successfully carried out, also the temperature of the blown metal passing from the converters to the open hearth is of great importance. To obtain maximum capacity in the open hearth, just as soon as it is ready for the blown metal, the blown metal from the converter should be ready to be poured in; and when the kicker charge is introduced, the bath should be at the proper temperature for the reactions to take place in the proper order. It should not be necessary to raise or lower the temperature of the heat very much. If the temperature of the molten bath in the open hearth is too high, the carbon is burned off first and after nearly all of it has been eliminated the phosphorus is oxidized and slagged. If the bath temperature is correct, the phosphorus reaction takes place first and the heat is finally worked down to the desired carbon content. Carbon is much more active in taking oxygen out of the molten metal than is phosphorus, with the result that when the process is carried out at the proper temperature and the heat is finished on carbon, the steel produced is much less likely to contain oxygen than when the heat is finished on phosphorus. The importance of this point, with respect to the bessemer stage, is that under certain conditions, already pointed out, the converters may furnish blown metal at an excessively high temperature which may be poured into an open hearth that, for various reasons, may be at a higher temperature than normal, with the result that the order of reactions in the open hearth is reversed and the open-hearth product may contain oxygen.

When running down at the end on phosphorus in this way, there is a twofold danger. If oxygen additions are made for the purpose of getting out the phosphorus, there is a chance that the steel will carry oxygen, although it may be thoroughly dephosphorized; whereas if there is not sufficient oxygen-carrying material charged to eliminate the phosphorus, the metal may not contain oxygen but it will not be dephosphorized. The alternatives then, when an open-hearth bath is finished on phosphorus, are that the metal either will be oxidized or the phosphorus will not be eliminated, whereas, if the order of reaction were changed and the phosphorus removed first and the carbon taken out at the end, the carbon would protect the metal from oxidation after dephosphorization and good steel would be produced.

It is not claimed that this happens in every open-hearth heat, but it does happen in some. This sequence of happenings can be avoided and the possibility of oxygen-carrying steel being made will be cut down to a minimum if excessive blast pressures are avoided. This can only be done economically, in the opinion of the writer, if basic or neutral converter bottoms are employed. The use of these bottoms will avoid the high blast pressures and cut down the power cost by burning the carbon to monoxide. In accomplishing both of these, the production of overheated blown metal will be minimized and the possibility of producing oxidized steel will be very slight.

DISCUSSION

BRADLEY STOUGHTON, New York, N. Y.—The results described are in line with my experience some years ago at a bessemer steel works. We avoided a good deal of corrosion of the bottom when we prevented the formation of iron oxide immediately at the mouths of the tuyeres.

There is no question that the bessemer metal arrives at the open-hearth furnace much too hot. In one large steel works, when the metal from the bessemer converter was poured into the open-hearth furnace, which already contained about 150 tons of molten metal, the metal from the converters was so hot that, although it was held in the ladles a little while, the reaction was so violent when it struck the basic slag of the open-hearth furnace that the slag foamed out of the furnace in some cases. Anything that would tend to reduce the temperature of the metal would yield beneficial results in the open-hearth furnace and would aid dephosphorization. Phosphorus will leave the iron most quickly at the low temperature and carbon most quickly at the high temperature. If, therefore, you wish to get rid of phosphorus as rapidly as possible, the metal should go to the open-hearth furnace at a low temperature, which is just what Professor McCaffery has achieved.

Jos. W. RICHARDS,* Bethlehem, Pa.—I agree that the reaction in the bessemer converter is mostly the formation of iron oxide, yet that is not the only reaction. There are two points of view: Does the air oxidize the silicon and carbon directly or does it first oxidize the iron, which then oxidizes these impurities. I believe that each impurity is oxidized primarily in proportion to its affinity for oxygen and in proportion to the chemical mass of the impurity present, and that the reactions with iron oxide taking place are secondary.

It seems to me that it would be absolutely necessary to add a large amount of lime, or some similar substance, to prevent the iron oxide from rapidly corroding the basic lining, assuming that the basic lining is dolomite or magnesite; I cannot find out from the paper which it is. If these fluxes are added, there is an increased amount of slag, so that the remedy is probably more costly than the results achieved warrant.

* Professor of Metallurgy, Lehigh University.

BIOGRAPHICAL NOTICES

James Gayley

JAMES GAYLEY, distinguished iron and steel metallurgist and inventor, died at his home in New York City on Feb. 25, after an illness of several weeks due to a complication of diseases. Mr. Gayley was born at Lock Haven, Pa., on Oct. 11, 1855, his father being a native of the north of Ireland, who came to this country in early manhood and became a Presbyterian minister. James Gayley's boyhood was spent in Maryland, where he attended the West Nottingham Academy. He took the course in mining engineering at Lafayette College, graduating in 1876.

Mr. Gayley began his career as chemist for the Crane Iron Co., Catasauqua, Pa., at a salary of about $500 a year. Three years later he became superintendent of the Missouri Furnace Co., resigning to take charge of the blast furnaces of the E. & G. Brooke Iron Co., at Birdsboro, Pa.

In 1885, Mr. Gayley became connected with the Carnegie interests when he was put in charge of the furnaces of the Edgar Thomson Steel Works at Braddock, Pa., owned by Carnegie Brothers & Co., Ltd., which subsequently became the Carnegie Steel Co. He soon began to institute economies in all departments, especially in the matter of fuel consumption, introducing many appliances, both time-saving and money-saving, and was largely instrumental in developing American blast-furnace practice to a higher plane than had been reached before. He was the first to install charging bins for the raw materials at the blast furnaces and also installed the first compound condensing engine for supplying air blast to a blast furnace. At the ore docks of the Carnegie Steel Co. at Conneaut, Ohio, he installed the first mechanical ore unloader and designed a vessel construction adapted to the use of such unloaders. Mr. Gayley was promoted to be manager of the entire Edgar Thomson works, and later, in 1897, became managing director of the Carnegie Steel Co. When the merger which created the United States Steel Corporation was formed in 1901, he was made the first vice-president in recognition of his services, and did work of a most important character, having charge of the department of raw materials and their transportation. Mr. Gayley resigned from the Steel Corporation in 1908, and since that time was president of the American Ore Reclamation Co. and the Sheffield Iron Corporation, as well as director in other companies.

During his brilliant career, Mr. Gayley made many important contributions to the metallurgical industry. Among his inventions the "dry air blast" was probably the most important, its use resulting in important

fuel economy with a uniformity of furnace product previously unobtainable. The Franklin Institute awarded him the Elliott Cresson medal in 1908 for this inventon, and, in 1913, he received the Perkin gold medal for his iron inventions.

Among Mr. Gayley's gifts to Lafayette College was the laboratory

JAMES GAYLEY.

of chemistry and metallurgy known as Gayley Hall, presented in 1902.

Mr. Gayley made many important contributions to technical literature. Among those to the TRANSACTIONS are: A Chilled Blast-furnace Hearth, Development of American Blast Furnaces, with Special Reference to Large Yields, The Preservation of the Hearth and Bosh Walls of the Blast Furnace, and Application of Dry-air Blast to the Manufacture of Iron."

Mr. Gayley became a member of the American Institute of Mining Engineers in 1880; was manager, 1896–1898; served as vice-president,

1902–1903; as president, 1904–1905; as president of the Board of Directors, 1905–1911; and as director, 1905–1913. He was also a member of the American Iron and Steel Institute, the (British) Iron and Steel Institute and a number of clubs.

The following tributes by members of the Institute were published in *Iron Trade Review:*

E. H. Gary.—James Gayley was possessed of fine qualities of mind and heart. His education, general and technical, was superior; consequently he was well equipped to reach and hold a high place in the estimation of all who knew him. In business, he was eminently successful. He had no enemies, but hosts of friends. He was just and generous in the treatment of all his associates in business, particularly subordinates. As first vice-president of the United States Steel Corporation for many years, he was respected, trusted and loved. He was the recipient of many honors and fully deserved them all. As one who knew him intimately, I cherish his memory and grieve because of his death.

H. A. Brassert.—With James Gayley's death, the last chapter has been written in the life book of a truly remarkable man. However, his fame as the father of modern American blast-furnace practice will be engraved in monumental letters in the history of the iron and steel industry. We gratefully acknowledge our indebtedness to him for the inspiring example that he set for his followers.

Joseph W. Richards

JOSEPH WILLIAM RICHARDS, was born in Oldbury, Worcestershire, England, on July 28, 1864, of English-Scotch parents, Joseph and Bridget (Harvey) Richards. In 1871, he came to this country with his parents. He attended the public schools of Philadelphia, Pa., where his father was a manufacturing metallurgist, and in 1882, graduated from the Central High School with the degree of A. B. The same year he entered Lehigh University, from which he received the degree of A. C. (Analytical Chemist) in 1886; M. S. in 1891, and Ph. D. in 1893. His connection with the university was continuous from 1887 until his death, and he therefore adds another to the list of names of men prominent in the A. I. M. E. who have helped to develop Lehigh University to the important position which it now occupies in mining and metallurgical education in respect of world-wide fame. It is fitting to recall in this connection that Eckley B. Coxe, a founder of the A. I. M. E., four times its vice-president, and president in 1878–79, was literally a pillar of the university for several years prior to his death; Thomas M. Drown, founder, vice-president, secretary for 11 years, honorary member, and president in 1897, was president of Lehigh University from 1895 to 1904; and Henry S. Drinker, founder, manager, vice-president, and honorary member, was president of the university from 1905 to 1920. Doctor Richards was no less active in both institutions.

With the exception of the years 1886 to 1887, when he was superintendent of the Delaware Metal Refinery of Philadelphia, his professional life was devoted to the upbuilding of the metallurgical department of the university, in part through his continuous services as a member of the teaching staff, and in part through the international renown won for the department by his achievements as author, investigator, expert and recognized authority in metallurgy, especially the metallurgy of aluminum, metallurgical-chemical calculations, and electrometallurgy. He was assistant instructor in metallurgy and blowpiping in 1887; instructor, 1888–90; instructor in metallurgy, mineralogy and blowpiping, 1890–97; assistant professor, 1897–1903; professor of metallurgy, 1903–1921. He died at his home in Bethlehem, Pa., on Oct. 12, 1921, of heart failure.

To the A. I. M. E., for a continuous period of a dozen years, his services were equally loyal and effective. He was vice-president, 1910–11, and 1916–17; councilor, 1912; director, 1913–15; chairman of the Iron and Steel Committee, 1914–21; he was one of the framers of the Insti-

tute's present Constitution and By-Laws and of several of their subsequent revisions; an influential member of the Committee on Papers and Publications, to which he gave generously of his time and effort; and a representative of the Institute on several joint committees of engineering societies, such as Engineering Council, Engineering Foundation, Ameri-

JOSEPH W. RICHARDS.

can Engineering Standards Committee, Engineering Division of the National Research Council, Committee on Development of Activities of Engineering Societies, and others.

He was a member of the Naval Consulting Board from its formation in 1915, and one of its hardest workers in the very important service of preparing for, and prosecuting, the United States' share of winning the world war. Personally, I viewed with some alarm the strain put upon his health and strength during the heat of a Washington summer, and during a part of the terrible epidemic of influenza there, when he acted as Washington representative of the Naval Consulting Board, perform-

ing a labor so dry and fatiguing that few would have had the courage, and fewer still the energy, to undertake it. It was characteristic of Richards that, if he obligated himself to a joint task, he was always ready to perform more than his share of the labor involved.

He was one of the founders of the American Electrochemical Society; its first president, 1902–03, and secretary from 1907 to 1921. He was president of the Chemical Section of the Franklin Institute, 1897, 1899, and professor of electrochemistry, 1907–10. He was honorary member of the American Electroplaters' Association, and a member, officer, or commitee-man in several American and foreign technical societies and clubs. Among his other public services may be mentioned:

1897, member, U. S. Assay Commission; representative, Franklin Institute to International Geological Congress in Russia; 1899, member, Jury of Awards, Department of Chemistry National Export Exhibition, Philadelphia; 1915, member, Jury of Awards, chairman of Sub-jury on Metallurgy, Panama-Pacific International Exposition, San Francisco.

He was widely sought as legal expert in chemical and metallurgical cases and as advisor in industrial metallurgical and electrometallurgical operations. In 1893, he recieved a medal at the Columbian Exposition for an exhibit showing the metallurgy of aluminum.

Professor Richards' books include a treatise on aluminum (Professor Richards always insisted on spelling it aluminium), which first appeared in 1887, with subsequent revisions amounting practically to new books on the subject, and which is the established authority on this subject in English; and "Metallurgical Calculations," in three small volumes, which have been translated into German, French, Italian, Spanish and Russian. He also translated, from German or Italian, "Electrolysis of Water," "Electrometallurgy of Chromium," "Arrangement of Electrolytic Laboratories," "Electrolytic Production of Metallic Objects," and "Cementation of Iron and Steel."

His contributions to technical literature by monographs, publications of individual researches, and discussions of papers and researches of others have been many and valuable.

On March 12, 1887, Professor Richards married Arnamarie Gadd, of Hertfordshire, England. Mrs. Richards died in 1920. Three children survive them; two daughters, Evelyn Packer Richards and Mrs. Winifred H. Hommel, and one son, William Richards.

Professor Richards was very fond of travel, and, except during the years of the war, his recent summers were spent in Scandinavia, Southeastern France and Switzerland. He familiarized himself with the metallurgical practice of these countries, and was doubtless the best-informed American on the electrometallurgical industries of Europe.

In seeking the characteristics which have contributed most to Richards' success and distinction in the metallurgical world, one is puzzled

whether to give first place to a seemingly tireless capacity for painstaking work, or to a methodical, intelligent system of acquiring information in a wide circle of subjects and of accomplishing the work which this information indicated as the most important to be done. In reply to a question as to how he achieved so much work in his busy life, he said, "I always have a time for each task, and I stick religiously to my schedule." He had few interests outside his technical activities, but the most prominent of these was a sympathetic taste for music and languages. In his early life, he studied religion deeply, and in later years gave much thought to religious and philosophic subjects.

He was an efficient and inspiring teacher, even succeeding in stimulating his students to an interest in the drier and more tedious aspects of the subject, which every conscientious teacher is obliged to present. His nature was strongly individualistic, and, like Theodore Roosevelt, he did not formulate his standards from the average opinion of his friends and associates, but referred questions of right and duty to his own conscience, which was guided by intellectual honesty and a keen critical faculty. Especially in the last ten years of his life, this critical faculty was tempered by his habitual courtesy and consideration for others, making him fair and impersonal in controversy and debate, for which his wide knowledge gave him great proficiency. As a presiding officer, he gave dignity to a meeting and brought out the best from the assemblage.

Perhaps what endeared him most to his colleagues and associates was his quiet and gentlemanly courtesy, his unselfishness, and his willingness to serve in any capacity where his talents would be of use, even when no honor, of which he had already received so much, might be attached to the office.

BRADLEY STOUGHTON.

D. K. Tschernoff

DIMITRI KONSTANTINOVITCH TSCHERNOFF, was born in Petrograd, Russia, on Nov. 1, 1839, and died in Yalta (Crimea) in the south of Russia, on Jan. 2, 1921.

He obtained his early education in the Russian Gymnasium, corresponding to the American high school, and in the Technologic Institute. On graduation from this Institute in 1858, he was engaged as a professor of geometry and algebra and later became a librarian and superintendent of the museum in the same Institute. He also attended lectures in the mathematical physics section at the University of Petrograd from 1859 to 1862.

In 1866, Professor Tschernoff left the Technologic Institute and entered the employ of the Obouchoff steel plant, founded in 1863 for the manufacture of guns. Here he did his most important work on the heat treatment of steel, its crystallization and metallography.

In 1880, he left the Obouchoff plant and went to the south of European Russia, where he discovered and developed some rock-salt mines. This enterprise brought him a rather large fortune.

In 1884, he returned to Petrograd and during the next four years held several prominent positions in government departments. In 1899, he became professor of metallurgy in the Michael Artillery Academy, and retained that position until the time of the Russian Revolution.

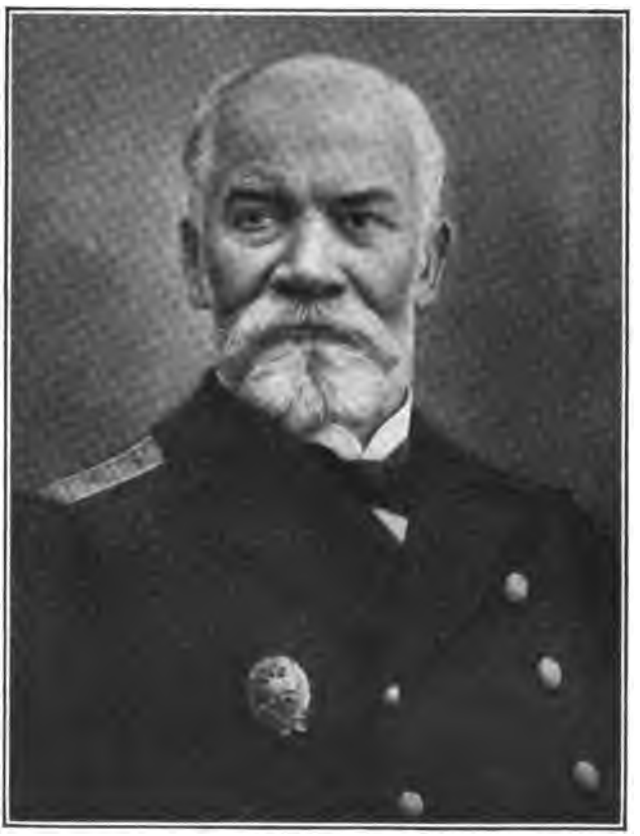
In 1902, Professor Tschernoff was elected an honorary member of the American Institute of Mining and Metallurgical Engineers.

In September, 1917, Professor Tschernoff was spending his vacation, as usual, in the city of Yalta (Crimea) in the south of Russia, with his wife and one of his daughters. The revolution progressed so rapidly that they were unable to return to Petrograd, and were compelled to stay in Yalta without provision for the winter season. Suffering from hunger and lack of sufficient clothing, and deprived of his books, Tschernoff nevertheless continued his studies and gave a number of lectures on steel at the Polytechnic Institute. At the same time he worked hard on some mathematical problems. His health broke down through long-continued under-nourishment.

His works in the metallurgical field are well known to the students of metallurgy; good abstracts of his most important papers were published in *Revue de Métallurgie* (1915, pp. 829–882) in commemoration of his 75th birthday.

Next to metallurgy, perhaps his greatest interest lay in astronomy, aviation and botany. Photography also claimed a large part of his interest and attention, and his favorite photographs were those he took of the frost on the windows of his conservatory. Some of the photographs in this wonderful collection were shown during his lectures on the crystallization of steel.

The construction of violins and violincellos also interested him. He



D. K. TSCHERNOFF.

advanced a theory that the fibers of the wooden boards forming the violin box should be arranged in a certain manner in order to obtain the best tonal value, and his violins, constructed in accordance with this theory, were tested in a large contest in Petrograd and were found to be of an excellent tone.

Professor Tschernoff led a very simple and modest private life, entirely devoted to his family and his works. His home, surrounded by a beautiful park, was in the remote residential part of Petrograd.

In spite of poor eyesight, which he injured while making his observations on the bessemer process, he was a hard reader. On the large table of his working chamber, were the latest books and magazines on various subjects, written in different languages. He was absorbed from early in the morning until late in the evening in his endless study, taking a respite for a short time by working in his garden or in his small machine shop. He allowed himself a good rest during only two days in each month.

Every other Sunday his house was open to his friends and his family acquaintances. In the evening of these Sundays, Tschernoff usually played chess, to which, like his old friend Mendeleieff, he was ardently devoted, and afterwards attended the family concert.

As in the case of a number of Russian scientists, the horrors of the revolution compelled him to live the last three years of his life under very miserable conditions, which broke his body but not his spirit, for, according to information received by the writer from his son, he continued his study and work up to the last moments of his life.

Though our dear friend, professor and scientist has passed away, his name and spirit will survive many generations.

A. I. KRYNITZKY.

Anders Richard Akerman

ANDERS RICHARD AKERMAN entered the eternal rest on Feb. 23, 1922, after a long and distinguished career. All mining men in Sweden are mourning him, because he was one of their greatest and a leader in the scientific metallurgy of the iron.

He was born April 18, 1837, in Stockholm, where his father, Joachim Akerman, was a professor at the Technical University, but the greater part of his childhood was spent in Falun, where the family moved after his father was made principal of the mining academy. He was at first taught by a tutor, but in 1851 entered the high school in Vesteras and the University of Uppsala in 1855, from which he graduated as a mining engineer on Dec. 11, 1860. A week later, he entered the service of the Department of Commerce and entered the mining academy at Falun, from which he graduated Dec. 15, 1862.

The following May, he was accepted as a student in the metallurgical section of "Jernkontoret" (the "Iron Institute") and on Oct. 22, 1864, he was made an assistant in the same section. Thus begun the coöperation with the Iron Institute which was to continue for so many years and to bear such rich fruit. He had, however, previously received two requests from the Iron Institute: One to assist Prof. V. Eggertz in the preliminary work of preparing a handbook on blast-furnace practice, the other to make a complete index of the proceedings of the Iron Institute ("Jernkontorets Annaler") volumes 1817–1864, which index was published in 1866.

On Oct. 19, 1865, Akerman was requested by "Jernkontoret" to give during 1866, lectures in the metallurgy of iron at the mining academy of Falun, as Prof. V. Eggertz wished to devote his entire time to the study of assaying. This request was renewed Oct. 15, 1867, for the year 1868, and on April 17, 1869, he was made instructor in metallurgy and mining at the Technical University, to which institution the higher education in mining engineering was transferred at that time. Akerman thus entered his career as a teacher, which lasted until the end of 1891. On May 11, 1877, he was appointed assistant professor in metallurgy and mining; on Sept. 7, 1883, he was appointed acting professor in the same department; and two weeks later was appointed dean of the mining college. On May 21, 1874, he was instructed by the Crown to inspect the mining schools in Filipstad and Falun. As a teacher, Akerman was very popular and his lectures were excellent, in form as well

as content. Though friendly and sociable, he always inspired respect. He distinguished himself particularly as a leader of the practical exercises.

At the request of the Jernkontoret, in company with Prof. C. A. Angstrom, he spent from July 20, 1866, to June 18, 1867, studying the iron industry of the United States, England, Scotland, France, and Austria. In July 1868, he visited the steel works in Upper Silesia, the Rhine Province, and Westphalia, accompanied by the master blacksmith, C. J. Boos.

On Oct. 19 of the same year he was requested by the "Jernkontoret" to become editor of the metallurgical department of "Jernkontoret's Annaler" (proceedings of the Iron Institute). After that date he wrote almost exclusively for "Jernkontoret's Annaler." Among his contributions to these proceedings were:

Preparation of Material for Siemens-Martin Steel-making Process.

Studies of Heat Conditions in Blast-furnace Process, Particularly with Regard to Influence of Hot Blast; this was translated, into German and English.

Ferries Self-coking Enclosed Blast Furnace.

Saving in Fuel Obtained by Use of High Blast Heat in Charcoal Blast Furnaces.

Composition of Gases Developed under Bessemer Process.

A Few Observations Regarding Heat Conditions in Blast-furnace Process.

Relation of Titanium and Tungsten to Iron and Their Influence on its Properties; this was translated into English and French.

Relation of Oxidized and Metallic Iron to Carbon Monoxide, Carbon Dioxide, Hydrogen and Water. This paper is mainly a resumé of the investigations of J. Lowthian Bell on equilibrium conditions between C, CO, CO_2, H_2, H_2O, Fe, and Fe_mO_n.

Influence of Silicon, Sulfur Phosphorus, and Manganese on the Properties of Iron and Conditions which Favor the Absorption as Well as the Removal of These Elements from the Iron; this was translated into English, German and French.

Viewpoints Concerning Grading and Stamping of Bessemer Metal of Different Kinds.

Views Regarding the Right Conception of the Term "Steel." This paper is directed against the suggestion that the term "steel" should cover all forgeable iron which has been produced in liquid form; he suggested the term ingot metal for such iron, which term was used at the Metallurgical Conference in Philadelphia in 1876.

Attempts to Investigate the Influence of Roasting on Magnetic Ore and Red Hematite.

Development of Swedish Iron Industry from 1860 to 1880, inclusive.

Comments on Caspersson's Bessemer Charts.

Reduction of Oxidized Iron by Means of Carbon Monoxide.

Different Heat Requirements for the Melting of Different Blast-furnace Slags.

Ash Contents and Percentage of Phosphorus in Wood and in the Charcoal Prepared from It.

Requirements for Suitable Production of Iron Castings and New Uses of Silicate Iron, which treats of the importance of the different elements Si, Mn, P, C, for different kinds of castings, cupolas and their operation; and silicate iron as an addition to pig iron in Bessemer converters.

History of Founding and Developing of Mining Schools in Sweden, which is to be found in the "Proceedings of 1817–1917" Memoir I

Among his contributions to the Proceedings of the Engineers' Society were:

Proposition for a Closed Blast-furnace Charging Bell and Cone.
Heaton's Method of Steel Manufacture.
About Heat Generation during the Bessemer Process.

On Aug. 25, 1871, he was requested by the government to be a member of the Swedish committee for the exhibition at Copenhagen in 1872, and on April 12, 1872, he was appointed judge at the same exhibition. He received similar commissions in connection with the world expositions at Vienna in 1873, Philadelphia in 1876, and Paris in 1878.

At the end of 1891, he left his position as teacher in the mining college to accept the position of general manager and chief of the Bureau of Commerce. Of this change he said. "Honored by the appointment by the Crown as chief of the Bureau of Commerce, my old activity as a teacher and scientist has ceased, and as to my new one all I have to say is that I hope that it may be useful to the government and the country." Akerman's connection with the Bureau of Commerce lasted until Jan. 20, 1905. During these 13 years, his time was occupied by many important public missions. He was appointed chairman of the committee for Sweden's participation in the World's Fair at Chicago, 1893; and later was made chairman of the committee for the distribution of purses for the visit of said exposition. He was chairman or member of several committees connected with the Fair in Stockholm in 1897, Paris in 1900, and St. Louis in 1904. On April 21, 1899, he was made chairman of the conference for international investigation of hydrography and biology of the waters around Norway, the North Sea, and the Baltic. On the same day that Akerman resigned from the Department of Commerce, he was appointed chairman of the Committee of Industrial Protection, the work of which terminated in 1909.

He continued to serve the Technical University as a member of its board from 1890 to 1908.

Among his other activities, the following deserve to be mentioned: Oct. 1, 1869–Oct. 1, 1874, he was librarian of the Technical University. 1874–1876, he was a director of Stora Kopperbergs Bergslag. In 1901, he became a director of Stora Kopperbergs Bergslags Aktiebolag; in 1911, its vice chairman; and in 1915, chairman of the Board of Directors (which office he held until 1917 when he resigned).

In 1889, he was made a director of the Swedish Life Insurance Co., Oden; 1895, its vice-chairman; and 1904, its chairman which office he held until his death.

He was vice-chairman of the Board of Directors in Stockholm-Vasteras Bergslagens Railroad 1897–1898, and chairman 1899–1917.

He was a director of Skandinaviska Kreditaktiebolaget 1901–1921.

He was one of the trustees of the Nobel Institute from 1902 and its vice-chairman from 1908 until his death.

He was chairman of the Letterstedt Society, from 1908 until 1921.

From 1894–1897 he was vice-chairman of the Board of the Technical University in Stockholm.

On Sept. 24, 1904, he was made chairman of the Board of Directors of Abraham Rydbergs foundation for the training of expert sailors, which office he resigned in 1918.

He received the following decorations and distinctions:

Chevalier Order of Dannebrog, Aug. 20, 1872.
Chevalier Order of Vasa, Dec. 1, 1873.
Chevalier Order of Franz Joseph, April 20, 1875.
Officer Legion of Honor, Oct. 19, 1878.
Chevalier Order of the North Star, Dec. 1, 1882.
Commander Grand Cross of the North Star, Nov. 30, 1901.
Commander Order of St. Olav of 1st Class.
Grand Officer Legion of Honor.
Chevalier of the Russian Order of St. Stanislaus, 1st Class.
Honorary Member of the Iron and Steel Institute of Great Britain, May 31, 1875.
Member of the Royal Swedish Academy of Science, Nov. 10, 1875.
Honorary Member of the New York Academy of Sciences, May 1, 1876.
Member of the American Philosophical Society, July 21, 1876.
Honorary Member of the American Institute of Mining Engineers, Nov. 1, 1876.
Member of the Royal Swedish Academy of Agriculture, April 15, 1878.
Honorary Member of the United States Association of Charcoal Iron Workers, Oct. 19, 1880.
Member of the Society of Science, Kristiania, 1892.
Honorary Doctor of the University of Uppsala, Sept. 6, 1893.
Honorary Member of the Royal Swedish Academy of Agriculture, 1909.
Honorary Member of the leading Russian Mining society, 1897.
Honorary Member of the Russian Metallurgical Society, June 18, 1911.
Honorary Member of the Academy of Engineering Sciences, 1920.
The Iron and Steel Institute Gold Medal, 1885.
The Great Gold Medal of the "Jernkontor," 1894.

Akerman was rather conservative with regard to the humanistic sciences and foreign languages. He was, however, a lover of paintings and in his old days he loved to procure large editions of fine books for his home, Mariahill at Djurgarden, the haven of rest to which he retired after his labors.

J. A LEFFLER.

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